4,9,14,19-Tetrafunctionalized Pagodanes de novo Synthesis – Functional Group Manipulations☆

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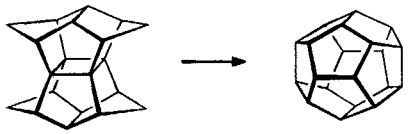
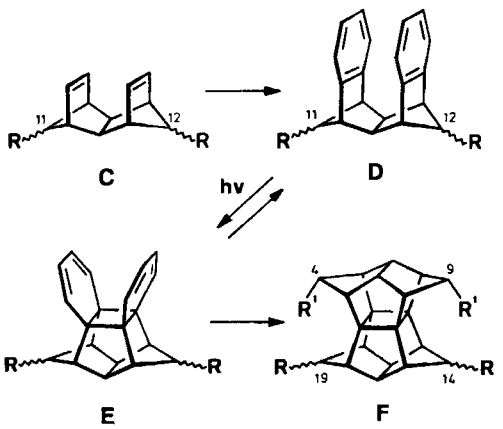
Various 4,9,14,19-tetrafunctionalized pagodanes are prepared by a de novo route commencing from appropriately substituted isodrin analogues (**3**, **4**). With the 14,19-dimethoxypagodane-4,9-dicarboxylic esters **30**/**31**, isolated after 16 one-pot operations (ca. 40 functional changes) in ca. 6.5% overall yield (ca. 84% per operation, ca. 93% per functional change), the scope for further functional group manipulations on the pagodane sphere is explored (e.g. diketone dicarboxylic ester **35**, dimethoxy diketone **37**, tetraketone **41**). In two face-to-face dibenzo substrates (**17**, **49**), clean photoequilibration with the corresponding *syn-o,o'*-dibenzo isomers (**19**, **50**) (75:25 and 80:20, resp.) is observed upon direct excitation (λ = 254 nm).

The [1.1.1.1]pagodanes play a central part in our quest for pentagonal dodecahedranes[1]. The Lewis-acid catalyzed transformation of the parent $(CH)_{20}$ hydrocarbons (**A**, **B**), though not sufficiently selective for extensive preparative utilization, was a first success[2]. Attempts to catalyze this transformation with the help of "super acids" led, instead, to the pagodane dication – the compensation being the latter's novel 2-electron σ-homoaromatic character[3,4]. The way out of this dilemma, e.g. directed stepwise procedures based on the high reactivity of the central four-membered ring in **A**, originally implied – as in the Paquette synthesis[5] – dehydrogenative transanular C–C bond formation at the bisseco- and secododecahedrane stages[6]. Thus experimental conditions were required, which allowed acceptable yields of the parent hydrocarbon, but posed a rather strict limitation to our early defined goal – the modification of the outer dodecahedrane sphere with diverse substitution patterns. In fact, previously incorporated functional groups generally did not survive these final bond forming procedures[7]. Yet, a broad spectrum of substituents would tolerate a variety of methods which are established for the formation of C–C bonds between sp^2 or between sp^2 and activated sp^3 centers. The non-trivial task to appropriately functionalize the pagodane framework at all four secondary positions (C-4, -9, -14, -19) was tackled on two independent tracks: Intramolecular functionalization at C-14(-19) by making use of the *syn*-4,*syn*-9 substituents in available pagodanes (**F**, R′ = H, R e.g. $CONH_2$)[8] and de novo synthesis starting not from isodrin but from adequately functionalized isodrin analogues[9].



A **B**

The latter approach, closely patterned after the original, systematically optimized pagodane synthesis[10], is detailed in this paper and subdivided into three stages. (i) The preparation of 11,12-disubstituted face-to-face dibenzo compounds **D** ([3.3]orthocyclophanes) from 11,12-disubstituted tetracyclododecadienes **C**, (ii) [6 + 6] benzo/benzo-photocycloaddition (**D** → **E**) and (iii) elaboration of the *syn,syn-o,o'*-dibenzo unit into the second pagodane cage (**E** → **F**). Implicit in the last stage are the *syn*-oriented functionalities (R′) at C-4(9) in **F**, leading to a simplification of the present project to the installation of the two functional groups at C-14(19) in **F** or at C-11(12) in **C**.

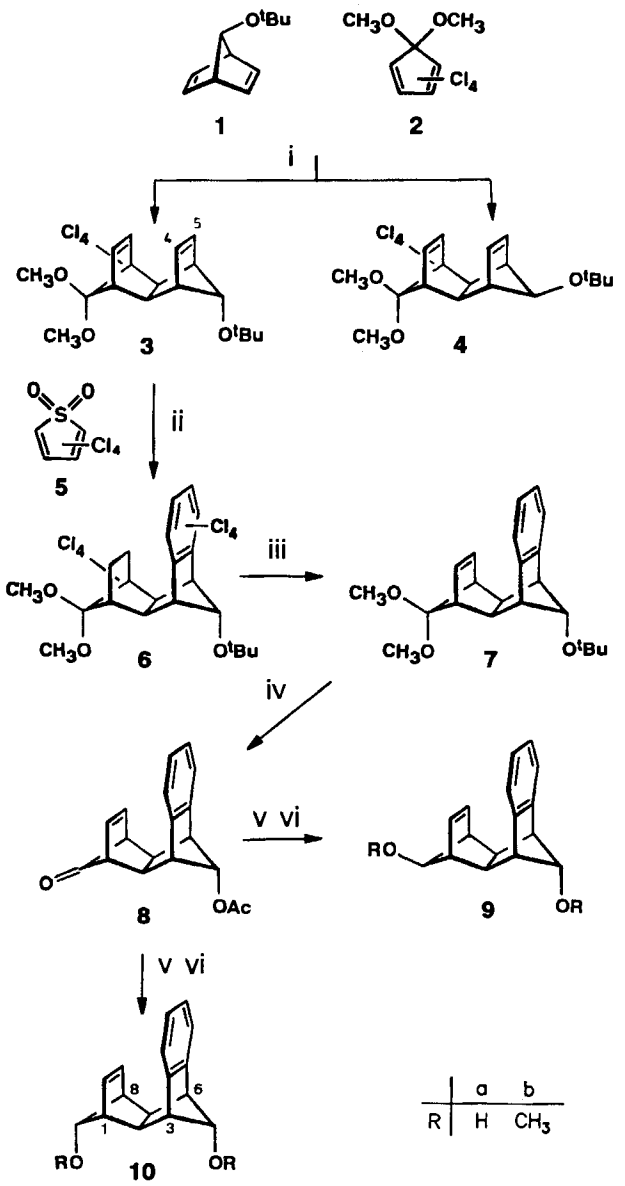


Face-to-face Dibenzo Substrates (D)

A general route to various 11,12-difunctionalized tetracyclododecadienes of type **C** is described in the literature[11,12]. In the end, our decision for specific substituents was made primarily under the aspect of their survival under the reaction conditions applied along the total route. After extensive experimentation we settled for the synthesis as outlined in Schemes 1 and 2 with the dimethoxy-*tert*-

butoxy compound **3** as starting material. It must be stressed that at this exploratory stage criteria like efficiency and total yield were not given absolute priority, yet. After small modifications of the literature procedure, from molar amounts of 7-*tert*-butoxynorbornadiene (**1**)[13] and tetrachlorocyclopentadienone dimethyl acetal (**2**)[14] 65% of the desired *endo,endo* adducts, 40% of **3** and 25% of **4**, are obtained together with ca. 12% of the *endo,exo* isomer of **4** and 5% of bisadduct. Separation on a molar scale by chromatography is expensive and time-consuming but is effected without significant loss of the relevant adducts **3** and **4**. Both **3** and **4** have been utilized for the construction of pagodanes. Only the reaction sequence based on **3**, however, is presented here in detail; the one starting from **4** is summarized below under "Complementary Results".

Scheme 1



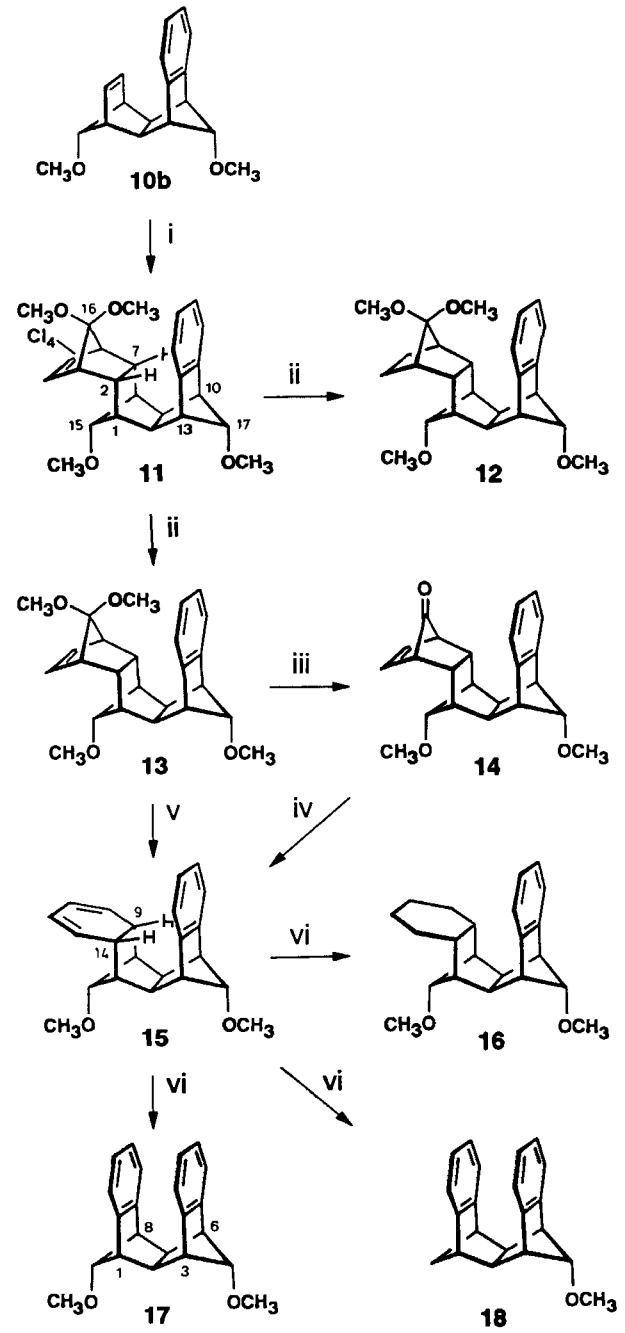
i: Toluene, 110°C/6 h. – ii: Toluene, 110°C/16 h. – iii: Na/*t*BuOH/THF, reflux/16 h. – iv: 85% $HClO_4$/HOAc/Ac_2O/CH_2Cl_2, 5°C → room temp./30 min. – v: $LiAl(OtBu)_3H$/THF, room temp./3 h. – vi: NaH/CH_3I/THF, room temp./12 h.

For the benzoanelation to the C4=C5 bond in **3** the C_4 synthon **2** proved of no use: In the resulting 1:1 adduct selective hydrolysis of just one of the two acetal units – of the carbonyl function to be eliminated on the way to **6** – was not possible. Use was therefore made of tetrachlorothiophene dioxide (**5**)[15]; as with **2**, exclusive addition to the C4=C5 bond in **3** could be assumed, since **3** had been found to be much less reactive than e.g. isodrin towards **2**. The uncertainty, though, remained, whether this addition could be brought about at temperatures which the thermally rather labile **5** would tolerate. In boiling toluene the still relatively slow but uncomplicated addition (16 h for total conversion) is followed by rapid loss of SO_2 and aromatization by dyotropic hydrogen transfer[16], this three-step one-pot sequence providing benzo intermediate **6** after crystallization from methanol in reproducible yields of 85% (molar scale). Removal of the eight chlorine atoms in **6** by treatment with sodium (not lithium)/*tert*-butyl alcohol[17] to give benzo/ene **7** poses no problem (91%). The latter, for obvious inductive and steric reasons, is absolutely resistant towards **2** and **5**. The second benzoanelation was therefore envisaged via *syn,syn*-dimethoxy benzo/ene **10b**, thereby also taking account of the observation that the O*t*Bu group was not totally retained in later steps. Sequential cleavage of acetal and ether functionalities in **7** and acetylation ($HClO_4$/acetic acid/acetic anhydride)[18] to give keto acetate **8** can be brought about under conditions, which are sufficiently mild (5°C) to exclude considerable CO elimination or skeletal rearrangements in the upcoming norbornenone and 7-hydroxy(acetoxy)benzonorbornane parts. The practically quantitative yield of **8** reached on small scales is, however, reduced to 80–85% on the molar scale. The thermal lability of **8** – CO elimination in boiling tetrachloromethane is complete after four hours – has to be considered in dealing with this compound. With the bulky $LiAl(OtBu)_3H$ reagent **8** is reduced at room temperature to a 1:10 mixture of *anti*/*syn*-diols **9a** and **10a** (83% isolated); after etherification with NaH/CH_3I the less soluble *syn* isomer **10b** can be easily separated by crystallization from methanol in 84% yield (m.p. 71°C). With respect to the stability of **10a** and **10b**, it must be kept in mind, that the close and *syn*-periplanar orientation of the unsaturated units (d = 2.81 Å, ω = 174.6° in the parent system[19]) make these systems prone to transanular reactions.

The second benzoanelation (**10** → **17**) was supposed to be executed in a manner similar to the first one, with **5** as the C_4 synthon. As has been reported earlier[10], the only feasible *exo* cycloaddition to the norbornene C=C bond in **10** generates strong steric compression for the two vinylic hydrogen atoms [9(10)-H], which are forced into the π cloud of the opposite benzene ring. It was open, to what extend steric repulsion exerted by the methoxy substituents in **10** would inhibit the *exo* addition and thus additionally raise the activation barrier. And indeed, even in boiling xylene addition of the diene **5** to **10b** proceeds relatively slowly but nevertheless with only minor decomposition. This route had

to be abandoned, however, when in the subsequent dehalogenation of the resulting adduct (cf. **6**) to **15** overreduction (i.a. **16**) could not be restricted to an acceptable extent. Fortunately, the reaction between **10b** and the less reactive diene **3**, though taking 48 hours in boiling xylene for completion, provides, with strict exclusion of air, an acceptable yield of ca. 80% of the adduct **11**; in the ^{1}H-NMR spectrum $\delta_{2(7)\text{-H}} = 2.26$ and $\delta_{15\text{-H}} = 3.84$ (cf. $\delta_{17\text{-H}} = 3.33$) are indicative of the congested steric situation. The latter might influence the course of the dehalogenation; under conditions, the application of which has allowed us to obtain 90% yield of **7**, **13** ($\delta_{2(7)\text{-H}} = 1.84$; $\delta_{15\text{-H}} = 5.14$) is constantly accompanied by up to 20% of the 4,5-dihydro derivative **12** and 5% of unidentified components. For **13** a somewhat tedious purification by crystallization (methanol) and chromatography is therefore needed. Both, two-phase acetal cleavage (dilute sulfuric acid, 92% of **14**, $\nu_{CO} = 1785$, 1760 cm^{-1}) and CO elimination (boiling CCl_4, 91% of **15**) are straightforward. The last two steps can be simplified (95% of **15**) by effecting acid-catalyzed transacetalization and decarbonylation by boiling in butanone[10].

Scheme 2



i: $C_7H_6O_2Cl_4$ (**2**)/xylene, 140°C/48 h. — ii: Na/*t*BuOH/THF, reflux/16–24 h. — iii: 30% H_2SO_4/CH_2Cl_2, room temp./16 h. — iv: CCl_4, reflux/8 h. — v: *p*-tosOH/*n*-butanone, reflux/16 h. — vi: 5% Pd/C, 200°C/20 min.

The dehydrogenative aromatization **15** → **17** has turned out to be the expected critical point: The steric shielding of the two "inner" hydrogens ($\delta_{9(14)\text{-H}} = 1.90$) is presumably intensified by the methoxy substituents and the latter themselves are potentially subject to reductive elimination. Indeed, under the necessarily very forcing conditions (10% Pd/C, substrate/catalyst ratio 1:10, 250°C, 30 min[9,10]), cleavage of etheral bond — in addition to the usual C–C homolysis — becomes detrimental. After extensive experimentation with various commercial catalyst systems, a 5% Pd/C catalyst from Engelhardt at a substrate-to-catalyst ratio of 1:10 (10–15-g lots of **15**, 200°C, 20 min) gave the best results: By crystallization (methanol) and chromatographic workup of the mother liquor 45–55% of *syn*-11,*syn*-12-dimethoxy dibenzo substrate **17** (in toto 16% based on **3**) can be reproducibly separated from polymers. Besides, 6–8% of **16**, 2–5% of **18**, and several small fluorescent components (i.a. naphthalenes) are obtained. The enormous amount of the expensive catalyst is regenerated by heating to 250°C under high vacuum.

Concerning the almost 50% material loss in the last step and the choice of the starting materials, two points must be made: Various alternative methodologies for bringing about dehydrogenation in **15** once more[10] were found ineffective, and shortening the route by substituting **1** by the 7-methoxy derivative was indeed considered. Leaving open the question how a smaller 7-substituent in norbornadiene might influence the adduct ratio in the reaction with **2**, there is simply no expeditious way to this methoxy compound[13].

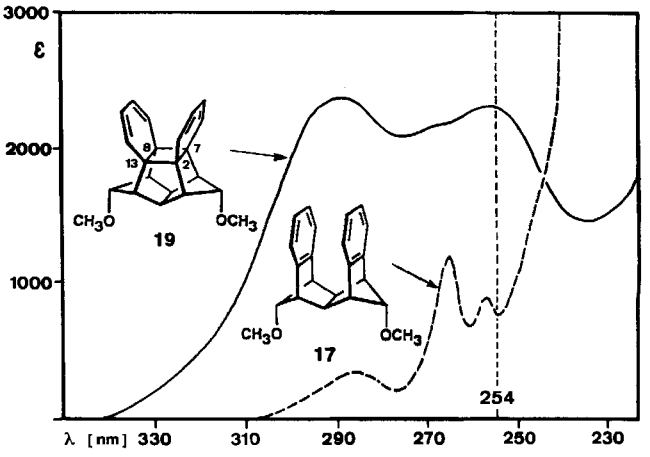
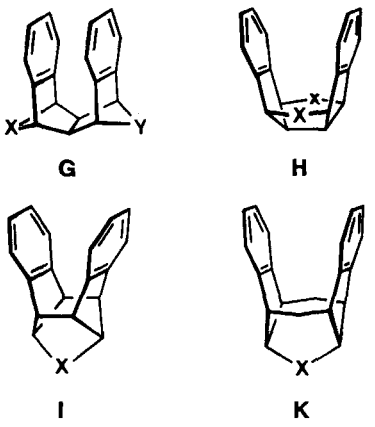


Figure 1. UV absorption curves of **17** and **19** (isooctane)

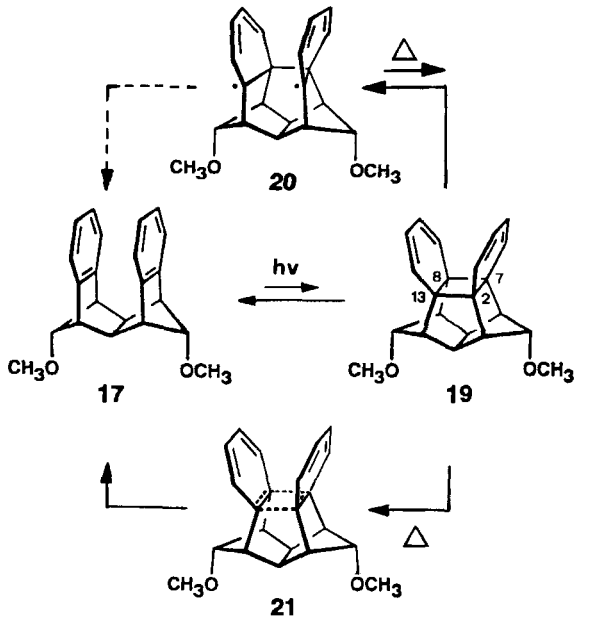
The face-to-face orientation of the two benzo rings in **17** with a closest $\pi-\pi$ distance of ca. 3 Å finds its usual expression in the ^{1}H-NMR and UV spectra. The signal of the aromatic protons (they are isochronous in $CDCl_3$) appears at relatively high field ($\delta = 6.59$), and the unstructured long-wavelength c.t. absorption band seems even slightly more red-shifted than in the parent hydrocarbon spectrum (Figure 1).

Benzo/benzo [6 + 6] Photocycloaddition (D → E)

The intramolecular [6 + 6] benzo/benzo photocycloaddition of type **D** → **E**, aspired in **17** (→ **19**), has been achieved for the first time for the bisdemethoxy parent compound of **17** upon direct excitation with monochromatic 254-nm light[19]. The failure to observe a photo product upon irradiation with different other light sources (wave lengths) and the 7:3 product ratio in the photoequilibrium has been – in a first approximation – correlated with the relative UV absorption intensities of the two photoisomers. By further work in the homologous series **G**[20–23] as well as with other specifically designed dibenzo substrates of type **H**[8,12,24], **I**[25] and **K**[26] a delicate structure dependency of this photocycloaddition reaction has been brought to light.



In the present context it must be remembered that in the **G** series the member with X = CH_2, Y = $(CH_2)_2$ like **17** (X = Y = CH_2) [not, however, the one with X = Y = $(CH_2)_2$ and not the diketone **55**[23]] undergoes [6 + 6] photocycloaddition[27]. Excluding the potential of the methoxy substituents in **17** to act as free rotors and thus to open a funnel for internal energy conversion in the otherwise very rigid molecular skeleton – an explanation provisionally advanced for the "photostability" of the **G** homologue with X = Y = $(CH_2)_2$[9,27] – good chances were seen for the formation of **19** as part in a preparatively useful photostationary equilibrium. Under slightly modified experimental conditions, **17** behaves as expected both with respect to rate and to specificity of the photoreaction. Irradiation of ca. 10^{-2} M deoxygenated cyclohexane solutions of **17** ($\varepsilon_{257\,nm}$ = 900) with the λ = 254 nm light from a low-pressure Hg lamp leads to a 75:25 equilibrium mixture with **19** ($\varepsilon_{255\,nm}$ = 2330). In preparative runs (Rayonet reactor, 15 g of **17** in 1.6 l of cyclohexane, which is chosen instead of isooctane for solubility reasons) the irradiation time for equilibration runs up to 12 h; yet, no thermal or photochemical side reaction interferes. After partial separation of **17** by crystallization (methanol), a careful chromatography (silica gel) is needed, however, in order to isolate 92% of **19** (based on converted **17**). This somewhat lengthy procedure is unavoidable, since a more convenient separation in a later step, as exercized in the original route[10], is not applicable here.



Crystalline **19** melts, when rapidly heated, unchanged at 170–171 °C; structure and symmetry are corroborated by the ^{1}H- and ^{13}C-NMR spectra. With respect to the, on first sight, surprisingly long-wavelength UV absorption (Figure 1) of such "benzene dimers", it has been concluded from PE- and X-ray studies[28] that this is mainly due to strong hyperconjugative through-bond interaction between the two cyclohexadiene chromophors. Upon irradiation with λ = 254 nm light **19** establishes the above equilibrium situation with **17**, with λ > 280 nm light it completely isomerizes back to **17**.

Benzo/benzo cycloadditions of the type **17** → **19** are highly endothermic and confer a substantial amount of strain to these bridged *syn-o,o'*-benzene dimers, the latter being nevertheless thermally rather stable ($\Delta\Delta H_f^0$ = 47.2 kcal/mol, $\Delta G^{\neq}$ (206 °C) = 38.2 kcal/mol for the unsubstituted analogue[10,29]). In fact, this property is one of the essentials of our synthetic scheme for pagodanes (dodecahedranes). For **19**, in a qualitative kinetic study in [D_6]benzene at 150 °C (^{1}H-NMR monitoring, sealed tube), a half-life of 30 min has been determined. In as much as the $\Delta G^{\neq}$ value of ca. 32 kcal/mol justifies any conclusion, the methoxy groups in **19** apparently exert a somewhat destabilizing influence. For the kinetic stability of the parent structure of **19** an explanation in terms of a structurally enforced concerted but symmetry-forbidden cycloreversion mechanism via an antiaromatic transition state (**21**), as opposed to a stepwise one (**20**), has been presented[29]. In view of the en-

ergetic margin, on which this classification is based, the argumentation should still hold for the present case.

Recently, the long missing $(CH)_{12}$ *syn-o,o'*-benzene dimer has been described[30]. In a comparison with the *anti* isomer[31] [$\Delta G^{\neq}$(25°C) = 26.7 ± 2.0 vs. 24.8 ± 1.0 kcal/mol] similar mechanistic arguments are invoked to account for the surprisingly higher kinetic stability of the *syn* dimer[30]. Thus, the cage effect in our bridged *syn-o,o'*-benzene dimers can be quantified to some 12(6) kcal/mol.

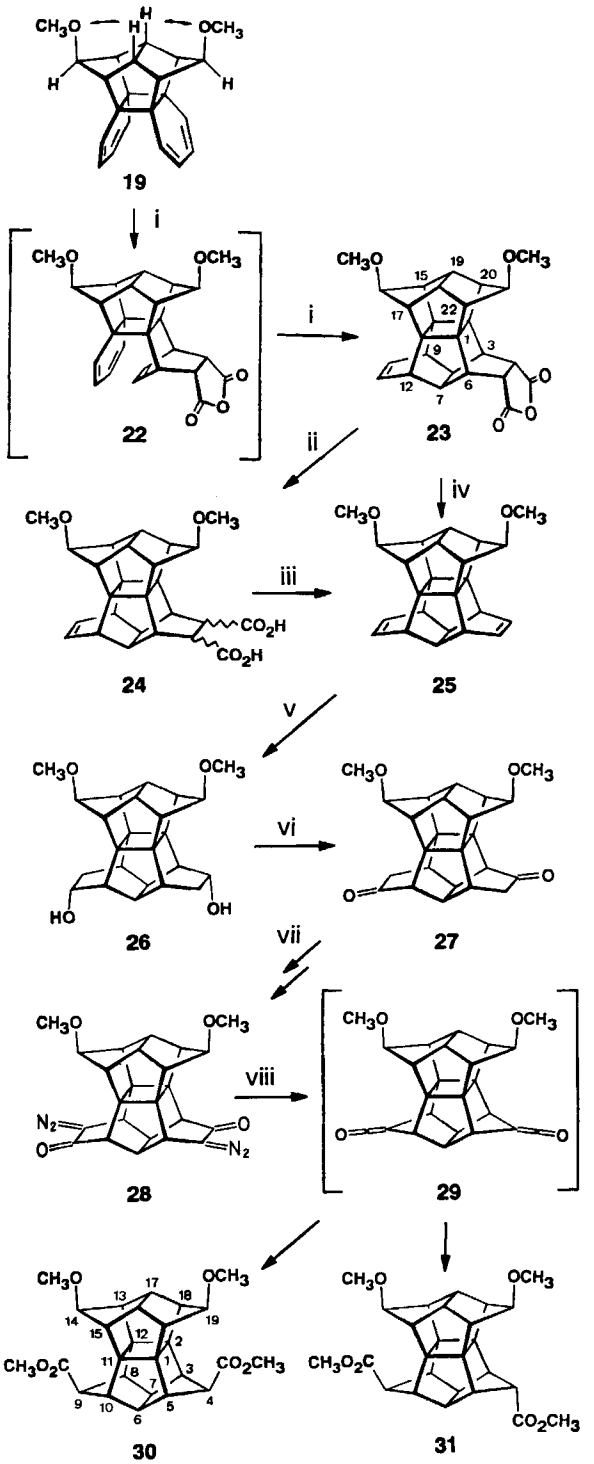
No mechanistic details of the still rather unusual benzo/benzo [6 + 6] photodimerization reaction[19-23,32] are available yet, no experimental information as to the relevant excited state(s) and as to the importance of initial charge transfer[33]. It is also unknown, whether the photoreversion **19** → **17** follows the adiabatic pathway established for the fragmentation of the parent *syn-o,o'*-benzene dimer[30].

To summarize the preparatively relevant aspects of this second stage: The need for the monochromatic 254-nm light source with its low light flux and the unfavourable equilibrium position make the production of larger amounts of **19** very time- and labour-consuming. Thanks to the absence of any photochemical side reactions, the overall yield, however, as stated for the first step (ca. 16% based on **3**), is only insignificantly affected.

4,9,14,19-Tetrasubstituted Pagodanes (F)

The conversion of the *syn-o,o'*-dibenzene part of **19** into the second bird cage unit of the [1.1.1.1]pagodane skeleton (**30**, **31**), delineated in Scheme 3, requires the construction of additional six cyclopentane rings. Two of them result from the domino-Diels-Alder reaction with maleic anhydride (MA) (**23**), the other four from the double photo-Wolff ring contraction on the [2.2.1.1]pagodane level (**28**). For the initial addition step **19** → **22**, the assumption of a somewhat higher activation barrier was primarily based on the consideration that steric shielding of the outer cyclohexadiene faces by the *syn*-15,19-hydrogen atoms, as a consequence of some buttressing between the 17(20)-hydrogen atoms and the CH_3O groups[10], would become more effective – in the worst case even giving an edge to the thermal retrocleavage **19** → **17** at consequently higher reaction temperatures. Another potential complication was seen in the improved situation for an inside pincer-type attack at **19**, as indeed had been realized with changing preference for sterically less demanding acetylenic dienophiles[34]. As it turned out, the MA addition to **19** needs no special thermal activation; at 100°C the reaction is complete after 16 h and provides exclusively the domino adduct **23** in optimal (>98%) yield. The principal features of the [2.2.1.1]pagodane skeleton **23**, C_s symmetry and *anti-cis* arrangement [*anti* (*syn*) with respect to the cyclobutane ring, cf. ref.[23] in ref.[10]] of the anhydride ring, are unambiguously demonstrated in the ^{1}H- and ^{13}C-NMR spectra. Mechanistically, the two-step pathway with intervention of **22** had been inferred from calculations[35] as well as from relative rate enhancements and stereoselectivities in related high-pressure versus ambient-pressure experiments[36]. The almost colinear σ alignment of the π lobes at a distance of possibly less than 2.9 Å in the intermediate **22** is certainly a good reason for the rapid collapse into **23**. The oxidative degradation of **23** to the dimethoxy

Scheme 3



i: MA/toluene, 100°C/16 h. – ii: KOH/CH_3OH, 120°C/12 h. – iii: Cu_2O/2,2'-bipyridine/quinoline, 155°C/2 h, 185°C/48 h. – iv: Cu_2O/2,2'-bipyridine/H_2O/quinoline, 140°C/16 h, 185°C/36 h. – v: B_2H_6/THF, 0°C → room temp./4 h, NaOH/H_2O_2, 0°C → room temp./2 h. – vi: Jones reagent/acetone, 0°C → room temp./2 h. – vii: HCO_2CH_3/NaH/THF/catalytic CH_3OH, room temp./16 h; *p*-tosN_3, room temp./CH_2Cl_2/8 h. – viii: CH_3OH, high-pressure Hg lamp, pyrex, room temp./4 h. Mixture of regioisomers.

Table 1. ^{1}H- and ^{13}C-NMR data ($CDCl_3$) for selected [1.1.1.1]pagodanes

	1-H (2,11,12)	3-H (5,8,10)	13-H (15,18,20)	4-H (9)	6-H (7)	14-H (19)	16-H (17)	CO_2CH_3	OCH_3
30	-	2.67	2.33	2.85	2.81	3.50	3.19	3.64	3.23
33	-	2.74	2.63	2.92	2.77	3.70	3.59	3.63	-
35	-	2.90	2.28	3.04	3.09	-	3.19	3.57	-
37	-	2.25	2.52	-	3.35	3.85	3.52	-	3.30
38b	-	2.28	2.28	3.69	2.55	4.46	3.24	-	3.20/3.27
44b	-	2.59	2.28	-	3.23	-	3.27	-	3.08/3.27
	C-1 (2,11,12)	C-3 (5,8,10)	C-13 (15,18,20)	C-4 (9)	C-6 (7)	C-14 (19)	C-16 (17)	CO_2CH_3	OCH_3
30	61.6	43.8	44.2	57.5	58.1	93.2	55.6	173.2/51.4	57.1
33	62.2	43.8	49.2	57.7	57.5	35.0	60.9	172.9/51.8	-
35	62.6	44.4	45.9	57.5	58.6	209.2	46.5	171.6/52.1	-
37	60.0	45.8	44.6	210.2	47.7	93.0	57.1	-	57.5
38b	61.9	44.2*	44.9*	90.7	50.6	93.8	56.3	-	56.5/57.2
44b	61.3	45.7	46.0	118.8	46.7	209.2	54.1	-	50.6/51.3

diene **25** proved more problematical than expected: After standard saponification, treatment of the resultant diacid mixture (98% **24**) with complexed Cu_2O in hot quinoline[37], the yield of **25**, crystallized from ether, never exceeded 56%. This relatively modest result could not be improved by modifying the degradation procedure, as e.g. treatment of **23** with Cu_2O in the presence of small amounts of water[10] or by change to conventional lead tetraacetate oxidation (20% **25**)[10,38]. Under the necessarily very drastic conditions, side reactions hampering the catalytic dehydrogenation **15** → **17** (C–C and C–O cleavage) are presumably intervening.

C_{2v} symmetry in the air-insensitive and thermally remarkably stable diene **25** (m.p. 224°C, $\nu_{C=C}$ = 1620 cm^{-1}) is reflected by the six ^{1}H- and seven ^{13}C-NMR skeletal signals. The following steps from the [2.2.1.1]pagodadiene **25** to the [1.1.1.1]pagodanedicarboxylic esters **30** (**31**) were straightforward. *anti*-Specific hydroboration of the two double bonds in **25** with a large excess of diborane – in order to prevent formation of insoluble polymeric alkylboranes – followed by oxidation provides after crystallization from methanol 86% of a statistical mixture of C_s and C_2 dimethoxy diols **26** (only one isomer is shown in Scheme 3). For the subsequent Jones oxidation the latter purification step may be omitted. Starting from the crude mixture of diols and inorganic salts the yield of C_s and C_2 dimethoxy diones **27** ($\nu_{C=O}$ = 1710 cm^{-1}) is nearly quantitative (94%, 97% from the isolated diols). Comparably efficient is the one-pot formylation/diazotization procedure leading to an oily 1:1 mixture of yellowish C_s and C_2 bisdiazoketones **28** (92%). For spectroscopic characterization the C_s isomer has been enriched (3:1) by repeated crystallization from methanol. After irradiation of a dilute CH_2Cl_2/methanol (ca. 1:10) solution of isomers **28** with the Pyrex-filtered light of a high-pressure mercury lamp ($\lambda > 280$ nm) to total conversion (the yellow colour vanishes, 3–4 h), the crude solid material according to NMR and TLC analysis consists of two monomeric components in a 9:1 ratio. After crystallization, their separation is effected chromatographically. Differentiation as C_{2v} and C_s symmetrical tetrafunctionalized pagodanes **30** (m.p. 276°C, 77%) and **31** (m.p. 195°C, 8%), respectively, primarily rests on the ^{1}H- and ^{13}C-NMR spectra (Table 1), which can be completely assigned by means of selective decoupling and NOE measurements. It must be recalled that in the pagodane skeleton the dihedral angles between methylene and vicinal bridgehead hydrogens are very similar [59.2° (*syn*) versus 65.0° (*anti*) in **1**] and do not vary much with substitution. The vicinal coupling constants are therefore correspondingly small and, if measurable at all, not very instructive. A direct manifestation of *anti*-positioned substituents is the deshielding of the neighbouring "ridge" hydrogens (6-, 7-, 16-, 17-H). Thus the 16(17)-H signal for **30** resonates at δ = 3.19 (3.22 for **31**) (Table 1), that for **A** at δ = 2.60. In control experiments, **30** and **31** are found to stay intact under the given reaction conditions, the protonation during addition of methanol to the intermediate ketenes (e.g. diketene **29**, though not probable) does not proceed therefore *anti*-specifically[39]. For **30** and **31** taken together, the overall yield for this third stage, starting from **19**, amounts to 41%. Thus, with the ca. 16% for the two preceeding stages, the overall yield for the multistep sequence starting from **3** is restricted to ca. 6.5%. Still, this means 84% per operation or 93% per functional change.

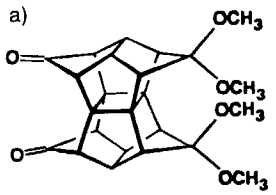
For reasons which have been detailed in another context[8,9], the R,R′ functionalities ear-marked for the final C–C bond formations on the pagodane (**F**) → dodecahedrane route (cf. **A** → **B**) have to be installed right at the pagodane stage, that is before reaching the (bis)secododecahedrane stages. With a supply of ca. 5 g of **30** and **31**, "scope and limitations" for functional group manipulations on the pagodane surface could be further explored – with special attention being paid to the introduction of sp^2-hybridized X,Y groups as e.g. the carbonyl functions in diketones **35**/**37** and tetraketone **41**. Previous limitations to such an endeavour have been caused by insufficient integrity of the central four-membered ring and by a lack of reactivity of "caged" *syn*-fixed substituents[8]. Some of the complications encountered in these preparations, specifically of **41**,

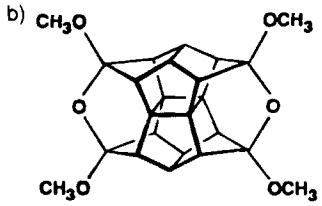
are directly related to the appreciable increase in strain energy, when in the [1.1.1.1]pagodane skeleton CH_2 units ($C-CH_2-C$ angle = 96.1°)[10] are substituted by C=O functions. ΔH_f^0 and E_{str} energies as calculated by MM2 (MM3)[40] have been of explanatory as well as exploratory help in our pagodane/dodecahedrane activities[1]. The relevant data for the parent pagodane (**A**), the 4,9-di- and the 4,9,14,19-tetraketone (**41**) as well as for dimethyl acetals derived from **41** are presented in Table 2. The strain increase in going from hydrocarbon **A** to tetrone **41** runs up to respectable 18 kcal/mol, with the increment per CO function increasing in every substitution. An unusually high tendency in **41** towards hydrate and acetal formation is the consequence. It is the steric situation in the pagodane half cages, however, which in the end determines the outcome of acetal (hydrate) formation: Clear favourites in the reaction with methanol are the diacetals **43** and **44**. The energetic compromise between counteracting hybridizational and compressional changes is inter alia recognizable in the 8 kcal/mol strain increase for the diacetal with two CH_3O groups being forced into the same pagodane half-cage, or in the ca. 5 kcal/mol strain decrease on going from the latter diacetal to the triacetal. The prediction is save in that transanular acetal (hydrate) formation (as in **45**) – that is insertion of O bridges between neighbouring CH_2 groups of the pagodane skeleton – is energetically no alternative.

First, we addressed ourselves to the task of converting the CH_3O substituents in **30** into potential *anti*-positioned leaving groups and thus to the problem to specifically cleave the etheral CH_3O bonds to obtain *anti,anti*-diol diester **32a**. From several methods investigated, the one using iodotrimethylsilane (TMSI)[41] and specified conditions (small excess, 0°C, 4 d), emerges as superior. The high yield of 93% crystalline **32a** achieved after methanolysis of bis(trimethylsilyl) ether **32b** is bound to the strict absence of free iodine in the reagent (colourless, freshly distilled[42]). In **32a**, the *anti*-OH groups are sterically easily accessible, thus esterification poses no problems. The prototypical bis(benzenesulfonate) **32c** is isolated in 85% yield (not optimized) under standard conditions. An unexpectedly expeditious access to the corresponding *anti,anti*-diiodide **33** (91%) was discovered in the treatment of **30** with a large excess of TMSI (10 equivalents) under reflux. Because of the strain increase connected with sp^2 hybridization at C-14(19) (**32'**), an explanation for the retention of configuration at these centers based on anchimeric assistance by the ideally placed *syn*-ester groups (**32''**) seems plausible. Insertion of two-atom bridges into the [1.1.1.1]pagodane skeleton as formulated in **32''** is energetically reasonable and has been experimentally verified[8,43]. An analogous S_Ni-type course seems also operative in the highly stereoselective halogen exchange taking place when diiodide **33** is exposed to excess bromine; besides *anti,anti*-dibromide **34**, isolated in 79% yield by crystallization, no other bromide can be detected (^1H NMR, TLC). With respect to the mechanism of the stepwise cyclobutane opening in pagodanes[1], the observation that **34** is formed with comparable selectivity by irradiation with the standard light source[10] is noteworthy. Iodine obviously quenches the bromine addition to the four-membered ring

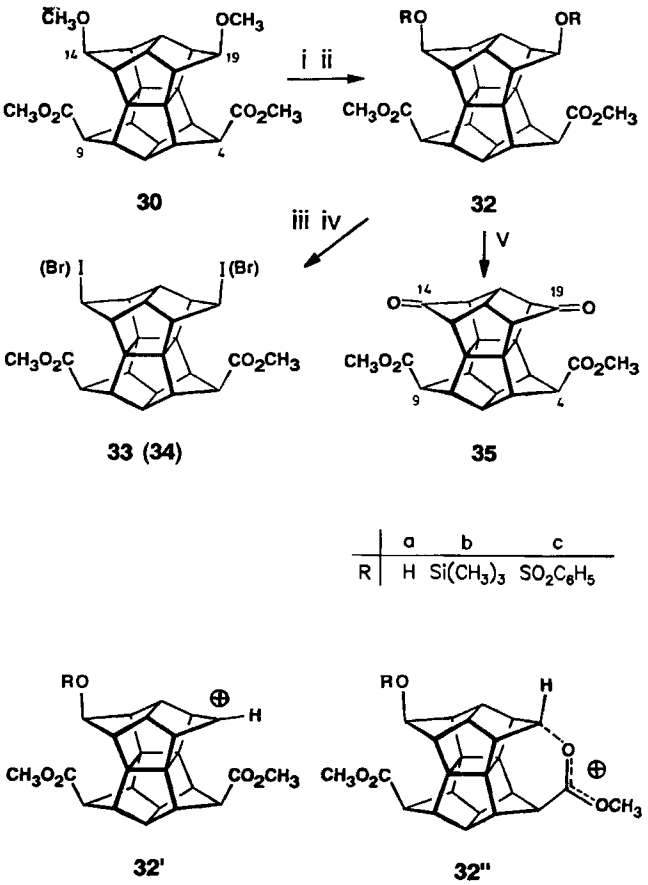
Table 2. Calculated (MM2) ΔH_f^0 and E_{str} energies (kcal/mol) for selected pagodane ketones and derived dimethyl acetals

	ΔH_f^0	E_{str}
A	64.4	115.0
4,9-Dione[10]	18.7	121.5
41	−22.10	132.80
Monoacetal	−82.50	124.20
43	−139.00	118.80
44	−139.60	118.90
4,19-Diacetal[a]	−131.60	126.90
Triacetal	−188.40	121.90
Tetraacetal	−210.90	153.50
45	−70.71	141.50
Bridged acetal[b]	−102.00	170.00

a) 

b) 

Scheme 4



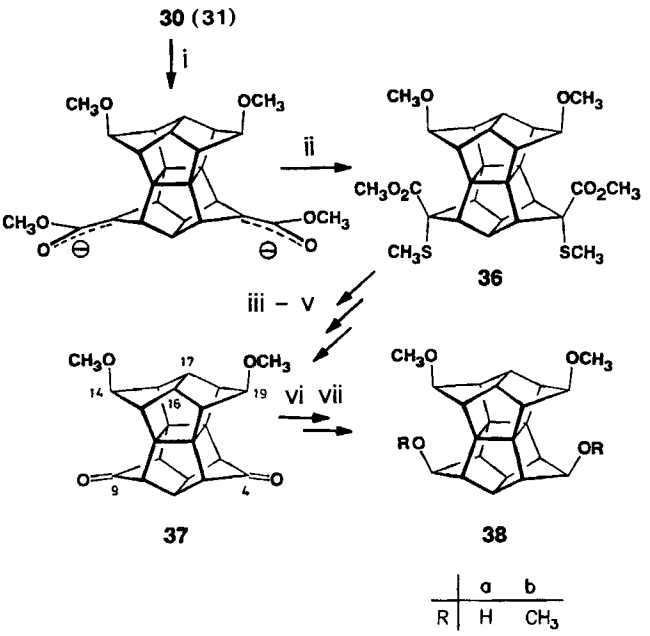
i: TMSI/$CHCl_3$, 0°C/4 days, CH_3OH. – ii: $C_6H_5SO_2Cl$/pyridine, room temp./24 h. – iii: TMSI/$CHCl_3$, reflux/24 h, CH_2N_2, room temp. – iv: Br_2/CH_2Cl_2, room temp./24 h. – v: Jones reagent/acetone, room temp./1 h.

whilst it is itself not added. As noted by Pinkos[8], in the absence of iodine the cyclobutane ring in dibromide **34** is amenable to (slightly modified) standard opening conditions.

High-yield oxidation of diol diester **32a** to dione diester **35**, with the *syn*-14,*syn*-19-hydrogens being hidden in the lateral pagodane caves, seemed not trivial in view of the problems faced in the dehydrogenation of **15**. Perhaps it is for this reason, that with various otherwise proven oxidizing reagents in aprotic medium (Collins[44], pyridinium chromates[45]) the results remained unsatisfactory. Yet with the Jones reagent in aqueous acetone **35** is selectively formed and reproducibly isolated in 94% yield after crystallization from CH_2Cl_2/methanol; the needles melt at 315–316°C without decomposition. Hydrate or acetal formation, sterically anyway only feasible with participation of the neighbouring ester groups, is no problem in dealing with **35**. Because of the acidity of the medium in the Jones oxidation procedure, the bissilyl ether **32b** as arising from the cleavage of **30** can be directly used[46], making the isolation of the hardly soluble diol **32a** unnecessary and shortening significantly the route to **35**. The strain in the norbornanone substructures of **35** manifests itself in the CO IR frequency of 1770 cm^{-1}, in the MS fragmentation pattern (100-% signal: m/z = 348 [M^+ – 2 CO]), and in the C_{2v} symmetry in the NMR spectra with five ^{1}H- and seven ^{13}C-NMR skeletal signals.

For the preparation of dimethoxy dione **37** from dimethoxy diester **30** (**31**), a slightly modified version[10] of the Trost method[47] once more proved as the one of choice. After complete twofold deprotonation of **30** at C-4(9) by LDA – controlled by the addition of triphenylmethyl anion indicator[48] – and stereospecific attack at 32^{2-} by the relatively voluminous dimethyl disulfide at 0°C, the *anti,anti*-bis(methylthio) derivative **36** is exclusively formed (TLC) and isolated in 94% yield. Starting from **31**, in order to suppress side reactions (i.a. amide formation with the more reactive *anti*-ester group), deprotonation has to be effected at –78°C at the expense of longer reaction times (5 h). With 82% **36** based on **31**, separation of the original **30**/**31** mixture is therefore not needed for the preparation of sterically uniform **36**. In the latter, because of strong steric interference between the ester groups and the opposite 14,19-hydrogen atoms – not similarly effective in **30** and **31** – C_2 and C_s symmetrical atropisomers are discernible in the NMR spectra at recording temperatures. This phenomenon might be taken as a manifestation for buttressing interactions of the kind formulated for **19**, here between "ridge" hydrogens (6-, 7-H) and CH_3S substituents. A cage situation tighter than in **30** is also held responsible for the very sluggish ester hydrolysis with **36**, which only in boiling ethylene glycol proceeds sufficiently rapid. After one-pot oxidation with *N*-chlorosuccinimide and acetal hydrolysis, crystalline C_{2v} symmetrical (NMR, Table 1) dimethoxy diketone **37** ($\nu_{C=O}$ = 1760 cm^{-1}) is collected after crystallization from CH_2Cl_2/ether in 88% yield in the form of colourless crystals, melting without decomposition at 219–220°C. As with **35**, there are no complications caused by hydrate formation. $LiAlH_4$ reduction of the ketone functions in **37** delivers hydride ions *anti*-specifically, as expected. For convenience, diol **38a** is characterized after alkylation as *syn,syn,anti,anti*-tetramethoxypagodane **38b**. Notable features in the ^{1}H-NMR spectrum (Table 1) are $\delta_{14(19)\text{-H}}$ = 4.46 [$\delta_{4(9)\text{-H}}$ = 3.69] as an expression of steric strain and $\delta_{16(17)\text{-H}}$ = 3.24 [$\delta_{6(7)\text{-H}}$ = 2.55] as a manifestation of the *anti*-position of the neighbouring OCH_3 groups.

Scheme 5

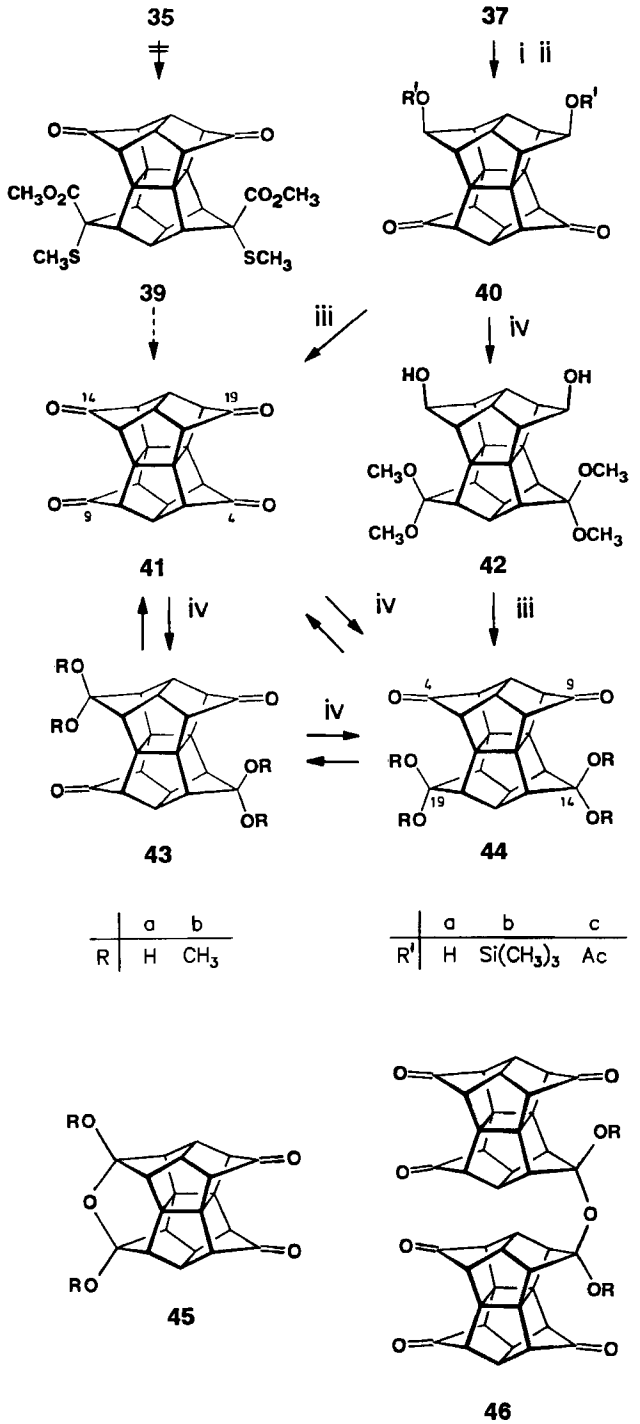


i: LDA/THF, –30°C → room temp./3 h. – ii: CH_3SSCH_3/1 h, room temp. – iii: KOH/ethylene glycol, reflux/24 h. – iv: NCS/CH_3OH/CH_2Cl_2, room temp./16 h. – v: HCl (concd.)/CH_2Cl_2, room temp./16 h. – vi: LAH/THF, reflux/1 h. – vii: NaH/CH_3I/THF, room temp./24 h.

With diketones **35**/**37** at hand, tetraketone **41**, a prominent pagodane derivative offering various synthetic options, seemed an easy prey – an illusion, as was quickly learnt. Application of the Trost method – so successful with **30** (**31**) – to **35** is wrecked at the thioalkylation step: Under various conditions, chosen in order to slow down intermolecular aldol-type competition reactions, repeatedly only trace amounts of **39** were detected among polymers. Obstruction by the carbonyl groups also complicates the conversion of **37** to **40a**, which is attempted under the conditions optimized with **30** (**31**). For whatever reasons and surprisingly in view of known ether cleavages in ketonic substrates[46], **37** does not react at all with TMSI at 0°C; higher reaction temperatures lead to complex product mixtures containing only minute quantities of **40a(b)**. After extensive experimentation with alternative procedures (i.a. acetyl chloride/$ZnCl_2$, acetic anhydride/$FeCl_3$[49]; NaI/H_3PO_4/acetic anhydride[50]) partial success was achieved with HBr/glacial acetic acid/acetic anhydride[51]. Under forcing conditions (120°C, pressure flask) from a slowly (16 h) evolv-

ing complex product mixture, after acetylation, the major component (50%) crystallizes from ether/hexane and is identified as the desired diacetoxy diketone **40c** (m.p. 302–304°C; $\nu_{C=O}$ = 1760 cm^{-1}; $\delta_{14(19)\text{-}H}$ = 4.94). When the difficulties in the isolation and manipulation of tetrone **41** have been found to exclude its broader preparative utilization, the step **37** → **40** has not been optimized any more (e.g. by use of boron trihalides[52] or lithium thiolates[53]). Mild transesterification of **40c** (K_2CO_3, methanol, room temperature, 0°C) furnishes quantitatively the diol diketone **40a**, a microcrystalline, hardly soluble powder, m.p. >320°C, which crystallizes from CH_3OH/CH_2Cl_2 and is sufficiently soluble in [D_6]DMSO for ^{1}H- and ^{13}C-NMR spectroscopic characterization ($\nu_{C=O}$ = 1760 cm^{-1}, $\delta_{14(19)\text{-}H}$ = 3.97).

Scheme 6



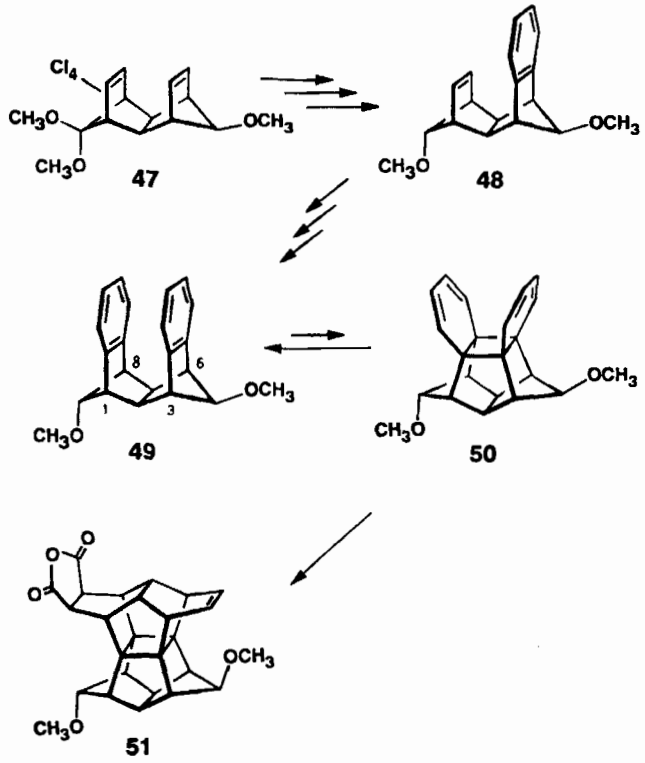
i: HBr/HOAc/Ac_2O, 120°C/16 h. – ii: K_2CO_3/CH_3OH, room temp./16 h. – iii: Collins reagent/CH_2Cl_2, room temp./1 h. – iv: *p*-tosOH/CH_3OH, reflux/48 h.

Oxidation of **40a** with CrO_3 in anhydrous pyridine/CH_2Cl_2 neatly produces a colourless solid, soluble in water and methanol, slightly in hot [D_6]DMSO, insoluble in CH_2Cl_2. ^{1}H-NMR analysis in – supposedly not perfectly anhydrous – [D_6]DMSO does, however, not allow to definitely identify the D_{2h} symmetrical **41** (with only two ^{1}H signals) among a rather complex mixture of hydrates. Attempts for thermal dehydration (150°C, 10^{-1} Torr) do not lead to a uniform product; intermolecular half-acetals of type **46** are probably involved. The at least transient presence of **41** is inferred from the reaction of the crude oxidation product with refluxing methanol/*p*-tosOH. The resulting solid residue (74% based on **40a**) is spectroscopically (IR, MS, ^{1}H and ^{13}C NMR) identified as a 7:4 mixture of the diketo diacetals **43b** and **44b**. By a reversed procedure the 7:4 ratio is established as thermodynamically controlled, and isomer **44b** is obtained in pure form. To this end, **40a** is first transformed into diol diacetal **42**, which, without purification, is oxidized under Collins conditions. From the finally homogeneous solution, **44b** [m.p. >320°C, $\nu_{C=O}$ = 1760 cm^{-1}; $\delta_{16(17)\text{-}H}$ = 3.27] is isolated in high yield (88% based on **40c**); it equilibrates in boiling CH_3OH/*p*-tosOH to the above cited 4:7 mixture with **43b** via several ^{1}H-NMR spectroscopically not distinguishable intermediates. Yet, even starting from uniform **44b** and using variously modified strategies for the acid-catalyzed acetal cleavage or transacetalization (i.a. against chloral under special water-binding precautions), we have never obtained the obviously extremely hygroscopic tetrone **41** without substantial amounts of different hydrates. Since **41** is a prototype of dodecahedrane precursors, in which final bond formations can be effected between sp^2 hybridized centres, the search for a sufficiently economic and efficient synthesis will be continued; progress in the strategy for functionality variation in pagodanes[8] could provide the necessary prerequisites.

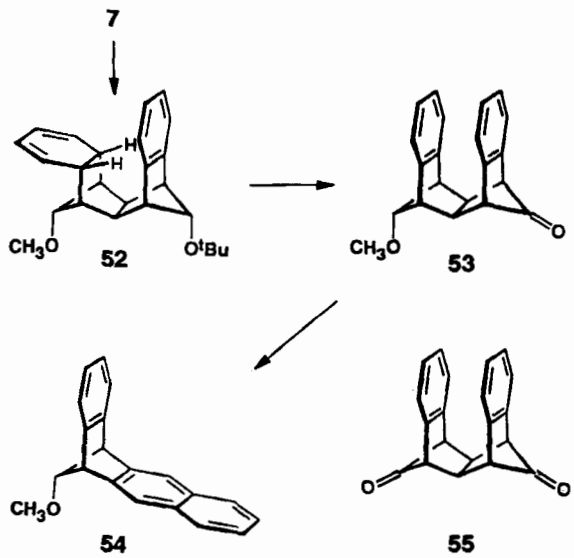
Complementary Results

Starting from **4**, the minor (25%) isodrin analogue of Scheme 1, in a synthetic route closely patterned after the one presented above for **17** in Schemes 1 and 2, we have prepared the face-to-face *syn*-11,*anti*-12-dimethoxy dibenzo substrate **49** via **47** and benzo/ene **48**. There are no significant discrepancies with regard to the course and outcome of the individual steps, and only the analytical data of relevant compounds are therefore listed for comparison in the experimental section. Two aspects deserve to be stressed, though: (i) The UV spectra of the phototautomers **49** ⇄ **50** closely resemble those of **17** ⇄ **19** (Figure 1), the photoequilibrium position has consequently been found to be very

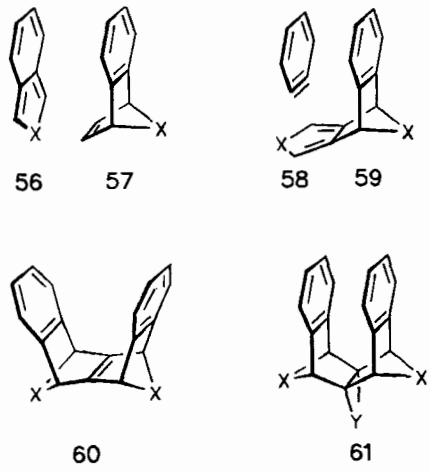
similar (80:20). (ii) The two cyclohexadiene units in *syn-o,o'*-dibenzene **50** can be perfectly discriminated in cycloaddition reactions. Steric protection of the cyclohexadiene side next to the *anti*-CH_3O substituent is such that MA adds exclusively to the other side to give domino adduct **51**. The latter has not been taken further on the route detailed for domino adduct **23** in Scheme 3.

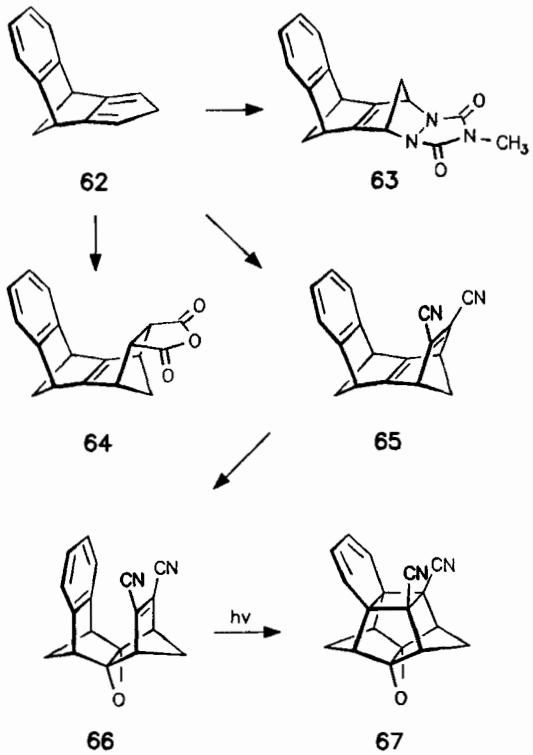


It has still to be explained, why the detour of replacing the *tert*-butoxy group in intermediate 7 (chart 1) was taken. After **52**, derived from 7, had been exposed to the dehydrogenation conditions, from a plethora of hydrogenated, dehydrogenated, non-fluorescent, and strongly fluorescent products the main one (up to 30%) was isolated and identified as the bridged dihydrotetracene **54**, supposedly arising from dibenzo methoxy ketone **53**. In the mixture of up to 10% of dibenzo compounds none contained *tert*-butyl groups (^{1}H NMR). Obviously, the *tert*-butyl/ether linkage does not survive the dehydrogenation step. The postulated intermediate **53** is known to us as a precursor in the generation of dibenzo diketone **55** from **17**. Compound **55** serves as a pivotal synthon for structure variations in the dibenzo series **G**. In irradiation experiments both with **53** and **55**, [6 + 6] benzo/benzo cycloaddition could not compete with CO extrusion[23].



Finally, the principal merits of the pagodane synthesis outlined here and which formally implies one C_{12} and two C_4 synthons shall be emphasized by shortly abstracting two alternative approaches to face-to-face dibenzo intermediates related to type **G** (**60**, **61**)[22]. These (X = CH_2 or O, NR),





twofold benzoanelated derivatives of the parent *syn*-sesquinorbornatriene[54], are expected to allow special substitution patterns as well as introduction of hetero elements in the final pagodanes. The (C_8X + $C_{10}X$) route (**56** + **57**) led, independently of the nature of the X elements, to [8 + 2] adducts of wrong stereochemistry, in line with prior studies[55]. On the (C_6 + $C_{12}X_2$) route (**58** + **59**), preparative limitations were already recognized in the preparation of the **59** components. With a small sample of the hydrocarbon **62** (**59**, X = CH_2) exploratory cycloaddition experiments could be performed: *N*-methyltriazoline-3,5-dione is exclusively added from the "bottom" (**63**), MA and dicyanoacetylene from the "top" (**64**, **65**). In close analogy to the parent hydrocarbon[54], the highly pyramidalized **65** is readily oxidized in the air to epoxide **66**, which upon exposure to an Osram 300-W daylight lamp undergoes [6 + 2] benzo/ene cycloaddition to give **67**.

Summary

The application of the (modified) original scheme for constructing the pagodane skeleton to the preparation of specifically polyfunctionalized derivatives was, in principle, successful. Thus, functionality modifications on the pagodane sphere and consequences of such functionalities to the next step en route to polyfunctionalized dodecahedranes, namely the opening of the four-membered ring (oxidation potentials[56]), could be further explored. Yet, there is a major deficiency of this de novo synthesis: The overall yield of ca. 6.5% for the tetrafunctionalized pagodanes **30** and **31** (based on **3**) is considerable lower than the ca. 30% yield achieved for the pagodane diester (based on isodrin) in the original route (**55** in ref.[10]). To a large extent, the material loss originates from two intrinsic steps (aromatization by high-temperature dehydrogenation, ene formation by oxidative decarboxylation), so that not much room is left for optimization. Clearly, wide-range applications in the dodecahedrane project are not in sight. Yet, the 11,12-difunctionalized dibenzo intermediates of this scheme (e.g. **17**, **49**) are broadly utilized for the preparation (via diketone **55**) of photomechanistically as well as preparatively valuable homologous and more or less rigid photosubstrates of type **G**. Fortunately, the breakthrough in our dodecahedrane project came from the alternative track towards 4,9,14,19-tetrafunctionalized pagodanes, in which the required functionalities are introduced only after reaching the pagodane stage[8,57].

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Experimental

Melting points (m.p.): Bock Monoscop M. – Analytical TLC: Merck silicagel plates with F_{254} indicator. – Flash chromatography: 0.04–0.06 mm silica gel, Macherey & Nagel. – Analytical GC: Varian 3700, glass capillary column 25 m, OV 17, FID; integrator Varian CDS 111. – ^{1}H NMR: Bruker WM 250, WM 400. – ^{13}C NMR: Bruker WP 80, WM 250, WM 400. Chemical shifts relative to TMS (δ = 0), coupling constants in Hz; if not specified differently the 250-MHz spectra are given; assignments denoted by * can be interchanged; assignments denoted by # refer to atropisomers. – IR: Perkin Elmer 457, Philips PU 9706. – UV: Perkin Elmer Lambda 15. – MS: Finnigan MAT 44S, EI, 70 eV, if not specified differently. – PE 30/50 = petroleum ether (30–50°C).

(1α,2β,3α,6α,7β,8α)-syn-12-tert-Butoxy-1,8,9,10-tetrachloro-4,5-(tetrachlorobenzo)tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-4-en-11-one Dimethyl Acetal (**6**): A solution of **3** (30.0 g, 70.0 mmol) and tetrachlorothiophene dioxide (**5**) (20.0 g, 78.8 mmol) in toluene (25 ml) is heated at reflux for 16 h with N_2 permanently bubbling through. After cooling to 50°C methanol (50 ml) is added, whereupon the product crystallizes from the yellowish solution. After 2 h at −20°C 37.0 g (85%) of **6**, colourless crystals with m.p. 277°C are obtained. – IR (KBr): $\tilde{\nu}$ = 2960 (C–H), 2920 (C–H), 2840 (C–H) cm^{-1}. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.72 (s, OCH_3), 3.69 (m, 2-, 7-H), 3.63 (s, OCH_3), 3.59 (m, 3-, 6-H), 3.57 (m, 9-, 10-H), 3.56 (m, 12-H), 1.20 [s, $OC(CH_3)_3$]. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 140.4 (C-1′, -2′), 131.8 (C-4′, -5′), 128.3 (C-3′, -6′), 109.9 (C-11), 88.3 (C-12), 75.8 [$OC(CH_3)_3$], 72.4 (C-1, -8), 59.7 (C-9, -10), 51.7 (OCH_3), 51.1 (OCH_3), 49.4 (C-2, -7), 49.2 (C-3, -6), 28.1 (3 CH_3).

$C_{22}H_{22}Cl_8O_3$ (618.0) Calcd. C 42.75 H 3.59
Found C 42.51 H 3.54

(1α,2β,3α,6α,7β,8α)-4,5-Benzo-syn-12-tert-butoxytetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-dien-11-one Dimethyl Acetal (**7**): A solution of **6** (117.4 g, 0.19 mol) in dry THF (1.5 l) and *tert*-butyl alcohol (281.2 g, 3.80 mol) is brought with stirring to the boil. Small pieces of sodium (104.9 g, 4.56 mol) are added in portions (3–5 g each) against a stream of N_2 to ensure constant boiling of the reaction mixture. After the addition is completed, the solution is heated to reflux for 12 h, then, after cooling to room temp., PE 30/50 (500 ml) is added. After pouring on ice (ca. 500 g) and extraction with ether, the organic phase is washed repeatedly with water, dried ($MgSO_4$), and concentrated in vacuo. The obtained uniform (TLC) colourless material is crystallized from methanol: **7** (59.0 g, 91%), colourless crystals, m.p. 99°C. – IR (KBr): $\tilde{\nu}$ = 3030 (arC–H), 2960 (C–H), 2845 (C–H) cm^{-1}. – UV (CH_3CN): λ_{max} (ε) = 279 nm (980), 274 (1000). – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.06 and 6.92 (AA′BB′, 3′-, 4′-, 5′-, 6′-H), 4.74 (m, 9-, 10-H), 3.53 (m, 12-H), 3.24 (s, OCH_3), 3.24 (m, 2-, 7-H), 3.02 (m, 3-, 6-H), 2.99 (s, OCH_3), 2.70 (m, 1-, 8-H), 1.22 [s, $OC(CH_3)_3$]. – ^{1}H NMR (C_6D_6): δ = 7.00 and 6.85 (AA′BB′, 3′-, 4′-, 5′-, 6′-H), 4.91 (m, 9-, 10-H), 3.57 (m, 12-H), 3.54 (m, 2-, 7-H), 3.14 (s, OCH_3), 3.06 (m, 3-, 6-H), 2.96 (s, OCH_3), 2.74 (m, 9-, 10-H), 1.06 [s, $OC(CH_3)_3$]. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 143.0 (C-4, -5), 126.6 (C-9, -10), 126.1 (C-4′, -5′), 122.9 (C-11), 122.5 (C-3′, -6′), 89.4 (C-12), 73.8 [$OC(CH_3)_3$], 51.5 (OCH_3), 49.7 (OCH_3), 50.2 (C-3, -6), 46.2 (C-1, -8), 41.9 (C-2, -7), 28.4 (3 CH_3).

$C_{22}H_{28}O_3$ (340.4) Calcd. C 77.61 H 8.28
Found C 77.35 H 8.01

(1α,2β,3α,6α,7β,8α)-syn-12-Acetoxy-4,5-benzotetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-dien-11-one (**8**): A solution of **7** (20.0 g, 58.8 mmol) in CH_2Cl_2 (20 ml), acetic acid (100 ml), and acetic anhydride (22 ml) is cooled to 5°C, then perchloric acid (12.0 g, 70%) is added quickly. After warming to room temp., the mixture is stirred for 30 min, poured on ice (1 kg) and extracted with CH_2Cl_2 (4 × 200 ml). The organic phase is washed with water (3 × 200 ml) and satd. $NaHCO_3$ solution (3 × 200 ml), dried ($MgSO_4$), and concentrated in vacuo. The solid residue is crystallized from ether: **8** (13.9 g, 84%), colourless crystals, m.p. 139°C. – IR (KBr): $\tilde{\nu}$ = 3060

(arC–H), 3020 (arC–H), 2980 (C–H), 2920 (C–H), 1765 (C=O), 1730 (C=O), 1220 (C–O) cm^{-1}. – UV (CH_3CN): λ_{max} (ε) = 278 nm (450), 273 (480). – ^1H NMR ($CDCl_3$): δ = 7.11 and 6.99 (AA'BB', 3'-, 4'-, 5'-, 6'-H), 5.06 (m, 9-, 10-H), 4.50 (m, 12-H), 3.50 (m, 3-, 6-H), 3.06 (m, 2-, 7-H), 2.90 (m, 1-, 8-H), 2.08 (s, $OCOCH_3$). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 197.2 (C-11), 170.2 ($OCOCH_3$), 140.3 (C-4, -5), 127.6 (C-4', -5'), 123.8 (C-9, -10), 123.2 (C-3', -6'), 85.1 (C-12), 49.7 (C-1, -8), 48.3 (C-3, -6), 39.0 (C-2, -7), 21.0 ($OCOCH_3$).

$C_{18}H_{16}O_3$ (280.3) Calcd. C 77.12 H 6.10
Found C 76.88 H 6.05

(1α,2β,3α,6α,7β,8α)-4,5-Benzotetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene-syn-11,syn-12-diol (**10a**): To a stirred suspension of $LiAlH_4$ (9.0 g, 237.2 mmol) in dry THF (500 ml), *tert*-butyl alcohol (52.7 g, 711.7 mmol) in dry THF (500 ml) is added dropwise under N_2. After 15 min to this suspension a solution of **8** (15.0 g, 53.5 mmol) in dry THF (500 ml) is added slowly at room temp. After 3 h water (9 ml), then aqueous NaOH (9 ml, 15%), and again water (27 ml) are added, the mixture is then stirred till the grey colour disappears and dried with $MgSO_4$ (20 g). The inorganic salts are removed by filtration, the solution is washed repeatedly with CH_2Cl_2/THF and the organic phase concentrated in vacuo. The resultant mixture of isomers **9a**/**10a** (1:10) is dissolved in CH_2Cl_2/methanol (1:2), filtrated over a small pad of charcoal (5 cm), and concentrated in vacuo. The solid residue is crystallized from CH_2Cl_2/methanol (1:1): 10.5 g (83%), m.p. 202°C. – IR (KBr): ṽ = 3260 (OH), 3060 (arC–H), 2950 (C–H), 2900 (C–H), 1100 (C–O) cm^{-1}. – UV (CH_3CN): λ_{max} (ε) = 279 nm (800), 272 (840). – ^1H NMR ($CDCl_3$/CD_3OD 1:1): δ = 7.04 und 6.92 (AA'BB', 3'-, 4'-, 5'-, 6'-H), 4.59 (m, 9-, 10-H), 3.87 (m, 12-H), 3.44 (m, 11-H), 3.34 (m, 3-, 6-H), 3.08 (m, 2-, 7-H), 2.39 (m, 1-, 8-H).

$C_{16}H_{16}O_2$ (240.3) Calcd. C 79.97 H 6.71
Found C 79.72 H 6.70

Etherification of **9a**/**10a**: A suspension of sodium hydride (3.6 g, 80% in mineral oil, 120 mmol) is washed in a N_2 atmosphere with *n*-hexane and dried in vacuo. After addition of dry THF (200 ml), a suspension of **9a**/**10a** (1:10) (12.0 g, 49.9 mmol) in methyl iodide (21.3 g, 149.9 mmol) and THF (200 ml) are added slowly, and the mixture is stirred for 12 h. After hydrolysis by careful addition of water (100 ml) at 0°C, the mixture is extracted with CH_2Cl_2 (4 × 100 ml). The organic phase is washed with water, dried ($MgSO_4$), and concentrated. From methanol pure **10b** (10.7 g, 80%) crystallizes. Additional **10b** (500 mg, 4%) and **9b** (1.1 g, 8%) are obtained by chromatography of the mother liquor (SiO_2, cyclohexane/ether 3:1).

(1α,2β,3α,6α,7β,8α)-anti-11,syn-12-Dimethoxy-4,5-benzotetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene (**9b**): Colourless crystals, m.p. 63–64°C (methanol). – IR (KBr): ṽ = 3060 (arC–H), 3040 (arC–H), 3020 (arC–H), 2960 (C–H), 2950 (C–H), 2920 (C–H), 1100 (C–O) cm^{-1}. – UV (CH_3CN): λ_{max} (ε) = 278 nm (680), 272 (730), 266 sh (550). – ^1H NMR ($CDCl_3$): δ = 7.00, 6.92 (AA'BB', 3'-, 4'-, 5'-, 6'-H), 4.69 (m, 9-, 10-H), 3.57 (m, 11-H), 3.32 (s, OCH_3), 3.29 (m, 12-H), 3.26 (m, 3-, 6-H), 3.12 (s, OCH_3), 2.92 (m, 2-, 7-H), 2.83 (m, 1-, 8-H). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 142.2 (C-4, -5), 126.5 (C-4', -5'), 126.2 (C-9, -10), 122.9 (C-3', -6'), 100.2 (C-11), 96.7 (C-12), 57.0 (OCH_3), 56.3 (OCH_3), 47.4 (C-3, -6), 46.9 (C-1, -8), 40.9 (C-2, -7).

(1α,2β,3α,6α,7β,8α)-syn-11,syn-12-Dimethoxy-4,5-benzotetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene (**10b**): Colourless crystals, m.p. 71°C (methanol). – IR (KBr): ṽ = 3060 (arC–H), 3030 (arC–H), 2980 (C–H), 2920 (C–H), 1100 (C–O) cm^{-1}. – UV (CH_3CN): λ_{max} (ε) = 279 (620), 273 (670). – ^1H NMR ($CDCl_3$): δ = 7.04, 6.92 (AA'BB', 3'-, 4'-, 5'-, 6'-H), 4.68 (m, 9-, 10-H), 3.48 (m, 12-H), 3.29 (s, OCH_3), 3.24 (s, OCH_3), 3.24 (m, 3-, 6-H), 3.20 (m, 2-, 7-H), 3.04 (m, 11-H), 2.54 (m, 1-, 8-H). – ^1H NMR (C_6D_6): δ = 7.00 und 6.82 (AA'BB', 3'-, 4'-, 5'-, 6'-H), 4.81 (m, 9-, 10-H), 3.48 (m, 3-, 6-H), 3.43 (m, 12-H), 3.15 (m, 2-, 7-H), 3.10 (m, 11-H), 3.07 (s, OCH_3), 3.01 (s, OCH_3), 2.53 (m, 1-, 8-H). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 143.2 (C-4, -5), 127.9 (C-9, -10), 126.4 (C-4', -5'), 122.7 (C-3', -6'), 99.0 (C-12), 98.1 (C-11), 56.3 (OCH_3), 55.9 (OCH_3), 46.9 (C-3, -6), 44.5 (C-1, -8), 43.0 (C-2, -7).

$C_{18}H_{20}O_2$ (268.3) Calcd. C 80.56 H 7.51
9b: Found C 80.41 H 7.32
10b: Found C 80.31 H 7.45

(1α,2α,3β,6β,7α,8α,9β,10α,13α,14β)-3,4,5,6-Tetrachloro-syn-15,syn-17-dimethoxy-11,12-benzohexacyclo[6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}]heptadeca-4,11-dien-16-one Dimethyl Acetal (**11**): A solution of **10b** (35.0 g, 0.13 mol) and **2** (37.9 g, 0.14 mol) in xylene (10 ml) is heated under N_2 at 140°C for 48 h (total conversion, NMR monitoring). After cooling to 80°C, the solution is diluted with methanol (50 ml) and then cooled with stirring to 0°C to give **11** (54.7 g, 79%) as colourless crystals, m.p. 193°C. Additional **11** (3.5 g, 5%) is obtained by chromatography of the mother liquor (SiO_2, CH_2Cl_2/CCl_4). – IR (KBr): ṽ = 2960 (C–H), 2910 (C–H), 2855 (C–H), 2810 (C–H), 1110 (C–O) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.24 (AA'BB', 3'-, 4'-, 5'-, 6'-H), 3.84 (m, 15-H), 3.34 (s, OCH_3), 3.33 (m, 10-, 13-H), 3.33 (m, 17-H), 3.32 (s, OCH_3), 3.26 (s, OCH_3), 3.14 (m, 9-, 14-H), 3.10 (s, OCH_3), 2.41 (m, 1-, 8-H), 2.26 (s, 2-, 7-H).

$C_{25}H_{26}Cl_4O_4$ (532.3)
Calcd. C 56.41 H 4.92 Cl 26.64
Found C 56.18 H 4.89 Cl 26.38

(1α,2α,3β,6β,7α,8α,9β,10α,13α,14β)-syn-15,syn-17-Dimethoxy-11,12-benzohexacyclo[6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}heptadeca-4,11-dien-16-one Dimethyl Acetal (**13**): To a boiling, efficiently stirred solution of **11** (46.0 g, 86.4 mmol) and *tert*-butyl alcohol (64.0 g, 0.86 mol) in dry THF (600 ml) sodium (24.0 g, 1.04 mol) is added in small pieces against a stream of N_2 in such portions (3–5 g each) as to ensure constant boiling of the reaction. Then the mixture is heated to reflux for 24 h, the remaining sodium forming a clotted mass. The mixture is cooled to room temp., diluted with PE 30/50 (400 ml), poured on ice (ca. 1 kg) and extracted repeatedly with ether. The combined organic phases are thoroughly washed with water, dried ($MgSO_4$), and concentrated in vacuo to give an oily raw mixture of **12**/**13** (ca. 1:4). After addition of methanol **13** (20.5 g, 60%) crystallizes, m.p. 143°C. Chromatography of the mother liquor (SiO_2, ether/*n*-hexane 1:1) gives additional 6.5 g (19%). – IR (KBr): ṽ = 3060 (arC–H), 3030 (arC–H), 2960 (C–H), 2940 (C–H), 2870 (C–H), 2810 (C–H), 1100 (C–O) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.17 and 7.13 (AA'BB', 3'-, 4'-, 5'-, 6'-H), 6.10 (m, 4-, 5-H), 5.14 (m, 15-H), 3.31 (s, OCH_3), 3.27 (m, 10-, 13-H), 3.27 (m, 17-H), 3.17 (s, OCH_3), 3.04 (m, 9-, 14-H), 2.89 (s, OCH_3), 2.64 (s, OCH_3), 2.51 (m, 3-, 6-H), 2.22 (m, 1-, 8-H), 1.84 (m, 2-, 7-H). – ^{13}C NMR ($CDCl_3$, 20.2 MHz): δ = 144.5 (C-11, -12), 135.8 (C-4, -5), 125.7 (C-4', -5'), 123.4 (C-3', -6'), 120.8 (C-16), 99.9 (C-17), 92.7 (C-15), 56.7 (OCH_3), 56.4 (OCH_3), 51.9 (OCH_3), 49.7 (OCH_3), 49.1 (C-2, -7)*, 47.3 (C-10, -13)*, 43.5 (C-3, -6)*, 42.1 (C-1, -8)*, 39.8 (C-9, -14)*.

$C_{25}H_{30}O_4$ (394.5) Calcd. C 76.11 H 7.67
Found C 75.89 H 7.52

(1α,2α,3β,6β,7α,8α,9β,10α,13α,14β)-syn-15,syn-17-Dimethoxy-11,12-benzohexacyclo[6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}]heptadeca-4,11-dien-16-one (**14**): A solution of **13** (20.0 g, 50.7 mmol) in CH_2Cl_2 (250 ml) is stirred with sulfuric acid (250 ml, 30%) at room temp. for 16 h. The organic phase is washed with water and satd. $NaHCO_3$ solu-

tion, dried ($MgSO_4$), filtrated over a short pad of silica gel, and concentrated in vacuo at 40°C to give 16.3 g (92%) of colourless crystals, m.p. 148°C (dec.) (ether/hexane 1:1). – IR (KBr): $\tilde{\nu}$ = 2990 (C–H), 2960 (C–H), 2950 (C–H), 2920 (C–H), 2860 (C–H), 2820 (C–H), 1785 (C=O), 1760 (C=O), 1110 (C–O) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.19 and 7.08 (AA'BB', 3'-, 4'-, 5'-, 6'-H), 6.43 (m, 4-, 5-H), 4.76 (m, 15-H), 3.38 (m, 17-H), 3.32 (m, 10-, 13-H), 3.30 (s, OCH_3), 3.16 (s, OCH_3), 3.10 (m, 9-, 14-H), 2.66 (m, 3-, 6-H), 2.39 (m, 1-, 8-H), 1.77 (m, 2-, 7-H). – ^{13}C NMR ($CDCl_3$, 20.2 MHz): δ = 198.1 (C-16), 143.9 (C-11, -12), 133.6 (C-4, -5), 126.1 (C-4', -5'), 123.8 (C-3', -6'), 99.6 (C-17), 91.4 (C-15), 56.9 (OCH_3), 56.4 (OCH_3), 51.8 (C-3, -6), 47.1 (C-10, -13)*, 44.6 (C-2, -7), 43.8 (C-9, -14)*, 37.7 (C-1, -8)*. $C_{23}H_{24}O_3$ (348.4) Calcd. C 79.28 H 6.94 Found C 79.00 H 6.83

(1α,2β,3α,6α,7β,8α,9α,14α)-syn-15,syn-16-Dimethoxy-4,5-benzopentacyclo[6.6.1.1^{3,6}.0^{2,7}.0^{9,14}]hexadeca-4,10,12-triene (**15**)

a) A solution of **14** (16.0 g, 45.9 mmol) in CCl_4 (500 ml) is heated to reflux for 8 h, then cooled to room temp., filtrated through silica gel (100 g), and concentrated in vacuo to give 13.4 g (91%) of colourless crystals (*n*-hexane).

b) A solution of **13** (7.0 g, 17.7 mmol), *p*-toluenesulfonic acid (150 mg, 0.9 mmol), and H_2O (0.5 ml) in butanone (30 ml) is heated to reflux for 16 h, then cooled to room temp., diluted with CH_2Cl_2 (100 ml), washed with satd. $NaHCO_3$ solution (3 × 50 ml), dried ($MgSO_4$), and concentrated in vacuo. The residue is filtrated through silica gel (CCl_4) to give colourless crystals (5.4 g, 95%), m.p. 154°C (*n*-hexane). – IR (KBr): $\tilde{\nu}$ = 3020 (arC–H), 2930 (C–H), 2880 (C–H), 2820 (C–H), 1110 (C–O) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.19 and 7.10 (AA'BB', 3'-, 4'-, 5'-, 6'-H), 5.45 (AA'BB', 11-, 12-H), 5.11 (AA'BB', 10-, 13-H), 4.10 (m, 15-H), 3.38 (m, 16-H), 3.34 (m, 3-, 6-H), 3.31 (s, 2 OCH_3), 3.09 (m, 2-, 7-H), 2.02 (m, 1-, 8-H), 1.90 (m, 9-, 14-H). – ^{13}C NMR ($CDCl_3$, 20.2 MHz): δ = 143.4 (C-4, -5), 128.6 (C-10, -13), 126.1 (C-4', -5'), 123.8 (C-3', -6'), 121.1 (C-11, -12), 99.5 (C-16), 93.9 (C-15), 57.2 (OCH_3), 56.4 (OCH_3), 48.9 (C-9, -14), 47.5 (C-3, -6), 43.2 (C-2, -7), 33.8 (C-1, -8).

$C_{22}H_{24}O_2$ (320.4) Calcd. C 82.46 H 7.55 Found C 82.19 H 7.36

Dehydrogenation of **15**: A mixture of **15** (12.0 g, 37.5 mmol) and Pd/C (120.0 g, 5%, Engelhard), homogenized by a ball mill, in three glass ampoules (3 × 25 cm) is repeatedly evacuated (10^{-1} Torr) and vented with N_2 and then, in a light stream of N_2, heated to 200°C for 20 min in a preheated oil bath. The mixture is then extracted continuously with ethyl acetate for 12 h, the organic phase filtrated through solid K_2CO_3 (20 g) and concentrated in vacuo to give a brown oil (9.5–11.5 g), which is dissolved in ether/cyclohexane (1:3). The solution is filtrated through silica gel (ca. 100 g). After concentration in vacuo the crude solid material is crystallized from methanol to give **17** (5.4–6.6 g, 45–55%) as colourless crystals (methanol). Chromatography of the mother liquor (SiO_2, ether/cyclohexane 1:3) provides 250–500 mg (2–5%) of **18** (R_f = 0.72) and 1.8–2.0 g of a mixture of hydrogenation products (R_f = 0.48). From this mixture 0.7–1.0 g (6–8%) of **16** is obtained as colourless crystals (methanol).

(1α,2β,3α,6α,7β,8α,9α,14α)-syn-15,syn-16-Dimethoxy-4,5-benzopentacyclo[6.6.1.1^{3,6}.0^{2,7}.0^{9,14}]hexadec-4-ene (**16**): M.p. 142°C (methanol). – IR (KBr): $\tilde{\nu}$ = 2960 (C–H), 2920 (C–H), 2850 (C–H), 2820 (C–H), 1110 (C–O) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.18 and 7.07 (AA'BB', 3'-, 4'-, 5'-, 6'-H), 4.04 (m, 15-H), 3.41 (m, 16-H), 3.33 (s, OCH_3), 3.31 (m, 3-, 6-H), 3.30 (s, OCH_3), 3.00 (m, 2-, 7-H), 1.91 (m, 1-, 8-H), 1.34 (m, 9-, 14-H), 0.95–0.77 (m, 10-, 11-, 12-, 13-H). $C_{22}H_{28}O_2$ (324.5) Calcd. C 81.44 H 8.70 Found C 81.71 H 8.89

(1α,2β,3α,6α,7β,8α)-syn-11,syn-12-Dimethoxy-4,5;9,10-dibenzotetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene (**17**): M.p. 161°C (methanol). – IR (KBr): $\tilde{\nu}$ = 3010 (arC–H), 2950 (C–H), 2870 (C–H), 1100 (C–O) cm^{-1}. – UV (isooctane): λ_{max} (ε) = 287 nm (330), 264 (1230), 257 (910), 228 (3440); ε_{254} = 900. – ^1H NMR ($CDCl_3$): δ = 6.59 (m, 3'-, 3''-, 4'-, 4''-, 5'-, 5''-, 6'-, 6''-H), 3.41 (m, 2-, 7-H), 3.34 (s, 2 OCH_3), 3.29 (m, 1-, 3-, 6-, 8-H), 3.20 (m, 11-, 12-H). – ^{13}C NMR ($CDCl_3$, 20.2 MHz): δ = 141.3 (C-4, -5, -9, -10), 126.1 (C-4', -4'', -5', -5''), 124.2 (C-3', -3'', -6', -6''), 99.4 (C-11, -12), 56.3 (2 OCH_3), 47.5 (C-1, -3, -6, -8), 40.7 (C-2, -7). – MS: *m/z* (%) = 318 (12) [M^+], 171 (75), 146 (96), 75 (100).

$C_{22}H_{22}O_2$ (318.4) Calcd. C 82.98 H 6.96 Found C 82.81 H 6.89

(1α,2β,3α,6α,7β,8α)-11-syn-Methoxy-4,5;9,10-dibenzotetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene (**18**): Colourless crystals, m.p. 108°C (methanol). – IR (KBr): $\tilde{\nu}$ = 3060 (arC–H), 3000 (C–H), 2950 (C–H), 2900 (C–H), 2860 (C–H), 1100 (C–O) cm^{-1}. – UV (isooctane): λ_{max} (ε) = 287 nm (310), 264 (1020), 257 (750), 228 (2680). – ^1H NMR ($CDCl_3$): δ = 6.62 and 6.55 (m, 3'-, 3''-, 4'-, 4''-, 5'-, 5''-, 6'-, 6''-H), 3.34 (s, OCH_3), 3.28 (m, 2-, 7-H), 3.26 (m, 1-, 8-H), 3.21 (m, 3-, 6-H), 3.20 (m, 11-H), 2.07 (dm, 12s-H), 1.80 (dm, 12a-H). – ^{13}C NMR ($CDCl_3$, 20.2 MHz): δ = 145.1 (C-4, -5), 140.5 (C-9, -10), 126.1 (C-4'', -5''), 125.4 (C-4', -5'), 124.3 (C-3'', -6''), 123.4 (C-3', -6'), 99.2 (C-11), 59.1 (C-12), 56.3 (OCH_3), 47.9 (C-1, -8)*, 46.2 (C-3, -6)*, 43.3 (C-2, -7)*. – MS: *m/z* (%) = 288 (12) [M^+], 171 (100), 116 (53).

$C_{21}H_{20}O$ (288.4) Calcd. C 87.46 H 6.99 Found C 87.81 H 6.89

anti-15,anti-19-Dimethoxyoctacyclo[12.5.1.0^{2,7}.0^{2,13}.0^{7,18}.0^{8,13}.0^{8,16}.0^{17,20}]icosa-3,5,9,11-tetraene (**19**): A solution of **17** (15.0 g, 47.1 mmol) in cyclohexane (spectroscopic grade, 1.6 l) in 10 quartz tubes (3 × 50 cm), purged with N_2 for 10 min, closed with a septum, is irradiated for 12 h (75:25 equilibrium mixture; ^1H NMR) in a Rayonet reactor with 254-nm light. Concentration in vacuo and chromatography on silica gel (7 × 60 cm, ether/petroleum ether 1:3) gives in the first fraction pure **17** (11.2 g, 75%, R_f = 0.50), in the second pure **19** (3.5 g, 23%, R_f = 0.34), colourless crystals, m.p. 170–171°C (*n*-hexane). – IR (KBr): $\tilde{\nu}$ = 3050 (arC–H), 3020 (arC–H), 2970 (C–H), 2920 (C–H), 2820 (C–H), 1100 (C–O) cm^{-1}. – UV (isooctane): λ_{max} (ε) = 290 nm (2400), 255 (2350), 215 (1830). – ^1H NMR ($CDCl_3$): δ = 5.74 (AA'BB', 4-, 5-, 10-, 11-H), 5.21 (AA'BB', 3-, 6-, 9-, 12-H), 4.19 (m, 15-, 19-H), 3.36 (s, 2 OCH_3), 3.15 (m, 17-, 20-H), 2.32 (m, 1-, 14-, 16-, 18-H). – ^{13}C NMR ($CDCl_3$, 20.2 MHz): δ = 125.5 (C-4, -5, -10, -11), 123.8 (C-3, -6, -9, -12), 91.7 (C-15, -19), 61.2 (C-2, -7, -8, -13), 57.4 (2 OCH_3), 56.5 (C-1, -14, -16, -18), 51.7 (C-17, -20). – MS (CI, NH_3): *m/z* (%) = 336 (35) [M^+ + 18], 287 (18), 255 (46), 171 (48), 146 (36), 75 (100). – MS: *m/z* (%) = 318 (1) [M^+], 171 (75), 146 (96), 75 (100).

Photolyses of **19**: A nitrogen-saturated solution of pure tetraene **19** (50 mg) in cyclohexane (20 ml) is irradiated with the 254-nm light for 3 h to give the above (25:75) mixture with **17** (^1H NMR). After irradiation of such a solution with light >280 nm (high-pressure Hg lamp, Pyrex filter) for 3 h **17** is isolated quantitatively (^1H NMR).

$C_{22}H_{22}O_2$ (318.4) Calcd. C 82.98 H 6.96 Found C 82.69 H 6.90

anti-16,anti-21-Dimethoxyundecacyclo[11.9.0.0^{1,6}.0^{2,14}.0^{2,20}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,17}.0^{15,19}.0^{18,22}]docos-10-ene-anti-4,anti-5-dicarboxylic Anhydride (**23**): A yellow solution of **19** (3.1 g, 9.7 mmol) and maleic anhydride (MA) (3.0 g, 30.0 mmol) in dry toluene (15 ml) is heated to 100°C under N_2 for 16 h, the solution becoming gradually colourless. Concentration in vacuo, removal of excess MA at 80°C/15 Torr and crystallization from methanol gives **23** (4.0 g, 100%), col-

ourless crystals, m.p. 208–209°C. – IR (KBr): $\tilde{\nu}$ = 2980 (C–H), 2950 (C–H), 2910 (C–H), 2880 (C–H), 1855 (C=O), 1770 (C=O), 1620 (C=C), 1230 (C–O), 1100 (C–O) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 6.13 (m, 10-, 11-H), 3.76 (m, 21-H), 3.60 (m, 16-H), 3.30 (m, 18-, 19-H), 3.30 (s, OCH_3), 3.22 (s, OCH_3), 3.03 (m, 4-, 5-H), 2.72 (m, 9-, 12-H), 2.37 (m, 3-, 6-, 20-, 22-H), 2.18 (m, 15-, 17-H), 2.03 (m, 7-, 8-H). – ^{13}C NMR ($CDCl_3$, 20.2 MHz): δ = 173.4 (2 C=O), 129.9 (C-10, -11), 93.3, 92.3 (C-16, -21), 58.8, 54.5 (C-1, -2, -13, -14), 57.2, 57.1 (2 OCH_3), 56.6 (C-18, -19), 46.2, 44.6, 44.5 (C-7, -8, -15, -17, -20, -22), 38.4, 38.3, 33.3 (C-3, -4, -5, -6, -9, -12). – MS: *m/z* (%) = 416 (84) [M^+], 171 (46), 146 (100), 131 (47), 103 (35), 75 (23).

anti-16,anti-21-Dimethoxyundecacyclo[11.9.0.0^{1,6}.0^{2,14}.0^{2,20}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,17}.0^{15,19}.0^{18,22}]docosa-4,10-diene (**25**)

1) *Two-step Procedure:* a) To a solution of **23** (5.0 g, 12.0 mmol) in methanol (75 ml) KOH (2.5 g, 44.6 mmol) in H_2O (10 ml) is added and the mixture heated in a bomb tube with a pressure relief valve to 120°C for 12 h. The clear solution is concentrated in vacuo, the semisolid residue dissolved in H_2O (50 ml) and the solution heated to 50–60°C, stirred, acidified with hydrochloric acid to pH 1, cooled to 0°C and the granular residue removed by filtration. The solution is washed with dist. H_2O and dried in vacuo (24 h, 10^{-1} Torr, P_2O_5) to give a mixture of diacids **24** as a beige powder (5.1 g, 98%).

b) *Degradation with Lead Tetraacetate:* To a solution of **24** (1.0 g, 2.3 mmol) in dry pyridine (15 ml) dried lead tetraacetate (2.0 g, 4.5 mmol) is added. After warming to 70–80°C for 10 min, then cooling to room temp. the solution is added to nitric acid (50 ml, 10%) and the mixture extracted repeatedly with CH_2Cl_2. The organic phase is washed with satd. $NaHCO_3$ solution, dried ($MgSO_4$), filtrated through silica gel, and concentrated in vacuo. The uniform solid residue is crystallized from ether to give **25** (220 mg, 28%).

b') *Degradation with Cu(I) Oxide:* A mixture of **24** (5.1 g, 11.8 mmol), Cu_2O (3.7 g, 25.9 mmol) and 2,2'-bipyridine (4.1 g, 26.2 mmol) in quinoline (25 ml) is stirred under N_2 at 155°C for 2 h, then at 185°C for 48 h. After cooling to room temp., CH_2Cl_2 (100 ml) is added. After filtration, the solution is washed three times with dild. hydrochloric acid, then with satd. $NaHCO_3$ solution, dried ($MgSO_4$), filtrated through silica gel (3 × 10 cm, cyclohexane/ethyl acetate 4:1, R_f = 0.32). After evaporation in vacuo the solid material is crystallized from ether: **25** (2.2 g, 54%).

2) *One-step Procedure:* A mixture of anhydride **23** (1.0 g, 2.4 mmol), 2,2'-bipyridine (410 mg, 2.6 mmol), Cu_2O (740 mg, 5.2 mmol), H_2O (2 ml), and quinoline (10 ml) is heated with stirring to 140°C for 16 h and, after removal of H_2O by distillation, to 185°C for additional 36 h. Workup as above and crystallization gives **25** (460 mg, 56%), colourless crystals, m.p. 224°C (ether). – IR (KBr): $\tilde{\nu}$ = 2990 (C–H), 2950 (C–H), 2930 (C–H), 2870 (C–H), 2820 (C–H), 1620 (C=C), 1100 (C–O) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 6.16 (m, 4-, 5-, 10-, 11-H), 3.69 (m, 16-, 21-H), 3.24 (s, 2 OCH_3), 3.21 (m, 18-, 19-H), 2.68 (m, 3-, 6-, 9-, 12-H), 2.19 (m, 15-, 17-, 20-, 22-H), 1.84 (m, 7-, 8-H). – ^{13}C NMR ($CDCl_3$): δ = 131.1 (C-4, -5, -10, -11), 93.0 (C-16, -21), 58.2 (C-1, -2, -13, -14), 56.9 (2 OCH_3), 56.7 (C-18, -19), 50.8 (C-7, -8), 45.8 (C-15, -17, -20, -22), 38.0 (C-3, -6, -9, -12). – MS: *m/z* (%) = 344 (98) [M^+], 280 (14), 197 (58), 147 (49), 146 (100), 131 (37), 115 (35).

$C_s(C_2)$-anti-16,anti-21-Dimethoxyundecacyclo[11.9.0.0^{1,6}.0^{2,14}.0^{2,20}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,17}.0^{15,19}.0^{18,22}]docosa-anti-4,anti-10(11)-diols (**26**): To a solution of **25** (4.0 g, 11.6 mmol) in dry THF (500 ml) a borane–THF complex (EGA, 1 M in THF, 26 ml, 26.0 mmol) is added under N_2 at 0°C. The mixture is stirred at room temp. for 4 h, then at 0°C cautiously aqueous NaOH (40 ml, 15%) and then H_2O_2 (26 ml, 30%) are added (exothermic reaction). The mixture is stirred at 0°C for 1 h and at room temp. for 16 h.

a) After addition of Na_2SO_3 (3.0 g) the mixture is stirred at room temp. for 15 min. The phases are separated, the aqueous phase is extracted repeatedly with THF, and the combined organic phases are concentrated in vacuo at 25°C. The solid residue (7.5 g), consisting of diols **26** (ca. 1:1) and inorganic salts, is used without further purification.

b) The aqueous phase is saturated with K_2CO_3 (40.0 g) and extracted continuously with CH_2Cl_2 for 24 h. Concentration in vacuo and crystallization of the residue from methanol provide the mixture of diols as colourless crystals (3.8 g, 86%), m.p. >320°C. – IR (KBr): $\tilde{\nu}$ = 3460 (OH), 2990 (C–H), 2950 (C–H), 2880 (C–H), 2820 (C–H), 1100 (C–O) cm $^{-1}$. – ^1H NMR (CD_3OD): δ = 3.86 (m, 16-, 21-H), 3.83 [m, 4-, 10(11)-H], 3.31 (s, 2 OCH_3), 3.24 (m, 18-, 19-H), 2.87 (m, 8*-H), 2.62 (m, 7-, 8-H), 2.36 (m, 7*-H), 2.25 and 2.21 (m, 15-, 17-, 20-, 22-H), 1.92 [m, 5s-, 10(11)s-H], 1.73 and 1.66 (m, 3-, 6-, 9-, 12-H), 1.49 [m, 5a-, 10(11)a-H]; in the ^1H NMR spectrum the 7-, 8-H signals of the C_2 isomer (*) are sufficiently separated to allow integration.

$C_{24}H_{28}O_4$ (380.5) Calcd. C 75.76 H 7.42
Found C 75.45 H 7.35

$C_s(C_2)$-anti-16,anti-21-Dimethoxyundecacyclo[11.9.0.0^{1,6}.0^{2,14}.0^{2,20}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,17}.0^{15,19}.0^{18,22}]docosa-4,10(11)-diones (**27**)

a) To the crude residue from the hydroboration reaction (ca. 11.6 mmol, mixture of isomers **26** with inorganic salts), dissolved in aqueous acetone (750 ml, 25%), within 30 min a mixture of CrO_3 (4.0 g, 40.0 mmol), H_2O (10 ml), and conc. H_2SO_4 (12 ml) is added at room temp. The mixture is stirred for 2 h, then CH_2Cl_2 (750 ml) is added, the phases are separated, and the aqueous phase is extracted with CH_2Cl_2 (2 × 250 ml). The combined organic phases are washed with H_2O and satd. $NaHCO_3$ solution (until decolouration), dried ($MgSO_4$) and concentrated in vacuo to give isomeric diones **27** (ca. 1:1) (4.1 g, 94% based on **25**) as colourless crystals.

b) To a suspension of **26** (300 mg, 0.79 mmol), isolated by extraction, in aqueous acetone (100 ml, 25%) a mixture of CrO_3 (210 mg, 2.1 mmol), H_2O (1 ml), and conc. H_2SO_4 (0.25 ml) is added within 30 min. Workup as above gives **27** (290 mg, 97%), m.p. 213–215°C (mixture). – IR (KBr): $\tilde{\nu}$ = 2950 (C–H), 1710 (C=O), 1100 (C–O) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 3.74 (m, 16-, 21-H), 3.40 (m, 18-, 19-H), 3.28 (s, 2 OCH_3), 3.06 (m, 8*-H), 2.84 (m, 7-, 8-H), 2.63 (m, 7*-H), 2.50–2.20 [series of m, 3-, 5-, 6-, 9-, 11(10)-, 12-, 15-, 17-, 20-, 22-H].

$C_{24}H_{24}O_4$ (376.4) Calcd. C 76.57 H 6.43
Found C 76.35 H 6.38

$C_s(C_2)$-5,11(10)-Bis(diazo)-anti-16,anti-21-dimethoxyundecacyclo[11.9.0.0^{1,6}.0^{2,14}.0^{2,20}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,17}.0^{15,19}.0^{18,22}]docosa-4,10-(11)-diones (**28**): A suspension of sodium hydride (2.1 g, 50% in mineral oil, 43.0 mmol) is repeatedly washed with hexane, then a solution of **27** (4.0 g, 10.6 mmol) in dry THF (200 ml) and thereafter methyl formate (2.6 g, 43.3 mmol) are added. The reaction is started by the addition of a small amount of methanol (0.1 ml). Two additional portions of methyl formate (2.6 g, 43.3 mmol) are added after 2 and 6 h, resp., and the reaction mixture is stirred at room temp. under N_2 for 12 h [total conversion, TLC control; ethyl acetate, R_f(**28**) = 0.47]. Then acetic acid (3.2 ml) and, after dilution with CH_2Cl_2 (40 ml), triethylamine (6.4 ml) and *p*-toluenesulfonyl azide (5.0 g, 25.4 mmol) are added. The mixture is stirred at room temp. in the dark for 6–8 h for total conversion (TLC control; with $FeCl_3$ no violet colouration), then diluted with CH_2Cl_2 (500 ml), washed with satd. $NaHCO_3$ solution (3 × 150 ml) and H_2O (3 ×

100 ml), dried ($MgSO_4$), and concentrated in vacuo. The yellow, oily residue is crystallized from methanol: **28** (3.1 g, 68%); yellowish crystals, m.p. 200°C (dec.). Additional 1.1 g (24%) is obtained by filtration of the mother liquor through silica gel (ethyl acetate). – IR (KBr): $\tilde{\nu}$ = 2950 (C–H), 2080, 1654 (C=O), 1380, 1100 (C–O) cm^{-1}. – C_s-**28**: ^1H NMR ($CDCl_3$): δ = 3.82 (m, 16-, 21-H), 3.41 and 3.38 (m, 18-, 19-H), 3.28 (s, 2 OCH_3), 3.18 (d, 6-, 12-H), 2.97 (dt, 8-H), 2.93 (dt, 7-H), 2.66 (d, 3-, 9-H), 2.45 (m, 15-, 17-, 20-, 22-H). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 193.3 (C-4, -10), 92.0 (C-16, -21), 59.6 (C-1, -2, -13, -14), 58.4 (C-5, -12)[#], 57.3 (2 OCH_3), 56.7 (C-1, -13), 56.4 (C-18, -19), 50.2 (C-8)[#], 49.3 (C-3, -9), 49.2 (C-7)[#], 45.6 (C-15, -20), 44.8 (C-17, -22), 35.3 (C-6, -12). – C_2-**28**: ^1H NMR ($CDCl_3$, 400 MHz): δ = 3.82 (m, 16-, 21-H), 3.38 (m, 18-, 19-H), 3.28 (s, 2 OCH_3), 3.11 (m, 6-, 9-H), 2.94 (m, 7-, 8-H), 2.77 (m, 3-, 12-H), 2.45 (m, 15-, 17-, 20-, 22-H). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 193.3 (C-4, -11), 92.0 (C-16, -21), 59.6 (C-2, -13), 58.7 (C-4, -10), 57.3 (2 OCH_3), 56.7 (C-1, -14), 56.4 (C-18, -19), 49.7 (C-7, -8), 48.7 (C-3, -12), 45.2 (C-15, -17)*, 45.1 (C-20, -22)*, 36.1 (C-6, -9).

$C_{24}H_{20}N_4O_4$ (428.4)
Calcd. C 67.28 H 4.71 N 13.08
Found C 67.03 H 4.48 N 12.77

Photolysis of **28**: 25 ml of a solution of **28** (2.0 g, 4.7 mmol) in CH_2Cl_2 (50 ml) is added to dry methanol (1 l). After saturation with N_2, the pale yellow mixture is irradiated with a 450-W Hg high-pressure lamp at room temp. (Pyrex filter) whereupon a crystalline material slowly precipitates. After complete decolouration of the solution (ca. 3–4 h), the second 25 ml of the **28**-solution is added and irradiated to complete decolouration. The precipitate is removed by filtration (pure **30**, 1.1 g, 53%). Concentration of the solution in vacuo and crystallization from CH_2Cl_2/methanol give additional 100 mg (5%) of **30**. Subsequent chromatography of the mother liquor (silica gel, CH_2Cl_2/ethyl acetate 2:1) yields **31** (165 mg, 8%, R_f = 0.61) and **30** (390 mg, 19%, R_f = 0.55). Thus, the total yield of **30** amounts to 77%.

Dimethyl anti-14,anti-19-Dimethoxyundecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane-syn-4,syn-9-dicarboxylate (**30**): Colourless crystals, m.p. 276°C (methanol). – IR (KBr): $\tilde{\nu}$ = 2980 (C–H), 1725 (C=O), 1250 (C–O), 1105 (C–O) cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): cf. Table 1. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): cf. Table 1. – MS: *m/z* (%) = 436 (79) [M^+], 405 (18), 376 (16), 285 (11), 239 (14), 128 (24), 115 (37), 75 (100).

$C_{26}H_{28}O_6$ (436.5) Calcd. C 71.54 H 6.46
Found C 71.22 H 6.40

Dimethyl anti-14,anti-19-Dimethoxyundecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane-syn-4,anti-9-dicarboxylate (**31**): Colourless crystals, m.p. 195°C (methanol). – IR (KBr): $\tilde{\nu}$ = 2970 (C–H), 2950 (C–H), 2820 (C–H), 1725 (C=O), 1240 (C–O), 1110 (C–O) cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 3.96 (m, 14-H), 3.65 (s, OCH_3), 3.64 (s, OCH_3), 3.51 (m, 19-H), 3.29 (s, OCH_3), 3.23 (s, OCH_3), 3.22 (m, 16-, 17-H), 3.02 (m, 6-, 7-H), 2.95 (m, 4-H), 2.85 (m, 9-H), 2.73 (m, 3-, 5-H), 2.50 (m, 8-, 10-H), 2.38 (m, 13-, 15-H), 2.34 (m, 18-, 20-H). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 173.7 (CO_2CH_3), 173.2 (CO_2CH_3), 93.5 (C-14), 93.4 (C-19), 61.7 (C-1, -2)*, 60.6 (C-11, -12)*, 58.9 (C-4), 57.5 (C-9), 57.5 (C-6, -7), 57.2 (2 OCH_3), 55.9 (C-16, -17), 51.5 (CO_2CH_3), 51.4 (CO_2CH_3), 44.9 (C-8, -10), 44.8 (C-13, -15), 44.4 (C-18, -20), 44.3 (C-3, -5). – MS: *m/z* (%) = 436 (100) [M^+], 405 (14), 376 (6), 285 (6), 253 (5), 221 (7), 158 (7), 128 (6), 115 (10), 75 (25).

Dimethyl anti-14,anti-19-Dihydroxyundecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane-syn-4,syn-9-dicarboxylate (**32a**): To a solution of **30** (200 mg, 0.46 mmol) in $CDCl_3$ (3 ml) freshly distilled iodotrimethylsilane (0.15 ml, 1.2 mmol) is added at 0°C in the dark with exclusion of moisture. After 4 d (NMR monitoring) at 0°C methanol (0.5 ml) is added, the slowly precipitating **32a** removed by filtration (160 mg, 85%) and the solution concentrated in vacuo. Chromatography of the oily residue on silica gel (CH_2Cl_2/ethyl acetate 4:1) yields additional **32a** (20 mg, 8%), total of 93% of colourless crystals, m.p. >320°C. – IR (KBr): $\tilde{\nu}$ = 3420 (OH), 2960 (C–H), 1725 (C=O), 1710 (C=O), 1240 (C–O) cm^{-1}. – ^1H NMR (CD_3OD/[D_6]DMSO): δ = 3.79 (m, 14-, 19-H), 3.58 (s, 2 OCH_3), 3.21 (m, 16-, 17-H), 2.88 (m, 4-, 9-H), 2.77 (m, 6-, 7-H), 2.52 (m, 3-, 5-, 8-, 10-H), 1.98 (m, 13-, 15-, 18-, 20-H).

$C_{24}H_{24}O_6$ (408.5) Calcd. C 70.58 H 5.92
Found C 70.32 H 5.99

Dimethyl anti-14,anti-19-Bis(phenylsulfonyloxy)undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane-syn-4,syn-9-dicarboxylate (**32c**): A solution of **32a** (65 mg, 0.16 mmol) and benzenesulfonyl chloride (135 mg, 0.76 mmol) in dry pyridine (3 ml) is stirred under N_2 at room temp. for 24 h. After addition of H_2O (50 ml) the mixture is extracted with CH_2Cl_2, the organic phase washed with dild. hydrochloric acid and satd. $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated in vacuo. Chromatography on silica gel (CH_2Cl_2) yields **32c** (92 mg, 85%), m.p. 255–256°C. – IR (KBr): $\tilde{\nu}$ = 2940 (C–H), 2885 (C–H), 1715 (C=O), 1365 (–SO_2–), 1240 (C–O), 1185 (–SO_2–) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 4.64 (m, 14-, 19-H), 3.70 (s, 2 OCH_3), 3.19 (m, 16-, 17-H), 2.85 (m, 4-, 9-H), 2.80 (m, 6-, 7-H), 2.64 (m, 3-, 5-, 8-, 10-H), 2.21 (m, 13-, 15-, 18-, 20-H).

$C_{36}H_{32}O_{10}S_2$ (688.8)
Calcd. C 62.78 H 4.68 S 9.31
Found C 62.58 H 4.57 S 9.28

Dimethyl anti-14,anti-19-Diiodoundecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane-syn-4,syn-9-dicarboxylate (**33**): A solution of **30** (270 mg, 0.65 mmol) and iodotrimethylsilane (0.8 ml, 6.5 mmol) in $CHCl_3$ (15 ml) is heated to reflux for 24 h in the dark with the exclusion of moisture. To the cooled (0°C), deep red mixture methanol (2 ml) and then a solution of diazomethane in ether is added, the mixture becoming colourless and then, with a small excess of CH_2N_2, slightly yellow. Concentration in vacuo and chromatography of the residue on silica gel gives 370 mg (91%) of colourless crystals; m.p. 221–223°C. – IR (KBr): $\tilde{\nu}$ = 2970 (C–H), 2945 (C–H), 1725 (C=O) cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): cf. Table 1. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): cf. Table 1. – MS: *m/z* (%) = 628 (50) [M^+], 501 (84), 469 (5), 441 (4), 374 (45), 314 (12), 191 (100).

Dimethyl anti-14,anti-19-Dibromoundecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane-syn-4,syn-9-dicarboxylate (**34**): A solution of **33** (200 mg, 0.32 mmol) in dry CH_2Cl_2 (100 ml) is stirred with bromine (4 ml, 78.1 mmol) at room temp. for 24 h (exclusion of moisture). Concentration in vacuo, filtration of the residue through silica gel (CH_2Cl_2) and crystallization (CH_2Cl_2) gives **34** (135 mg, 79%); m.p. 235–236°C. – IR (KBr): $\tilde{\nu}$ = 2970 (C–H), 2940 (C–H), 1725 (C=O) cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 3.84 (m, 14-, 19-H), 3.65 (s, 2 OCH_3), 3.59 (m, 16-, 17-H), 2.91 (m, 4-, 9-H), 2.81 (m, 6-, 7-H), 2.75 (m, 3-, 5-, 8-, 10-H), 2.60 (m, 13-, 15-, 18-, 20-H). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 173.0 (2 CO_2CH_3), 62.8 (C-1, -2, -11, -12), 69.1 (C-16, -17), 58.6 (C-14, -19), 57.8 (C-4, -9), 57.7 (C-6, -7), 51.9 (2 OCH_3), 48.5 (C-13, -15, -18, -20), 43.9 (C-3, -5, -8, -10). – MS: *m/z* (%) = 536 (64), 534 (100), 532 (63).

Dimethyl 14,19-Dioxoundecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane-syn-4,syn-9-dicarboxylate (**35**)

a) To a suspension of finely powdered **32a** (200 mg, 0.49 mmol) in aqueous acetone (100 ml, 25%) a mixture of CrO_3 (140 mg, 1.40

mmol), H_2O (0.6 ml), and concd. H_2SO_4 (0.12 ml) is added dropwise. The mixture is stirred at room temp. for 1 h, diluted with CH_2Cl_2 (100 ml) and the aqueous phase extracted with CH_2Cl_2 (3 × 50 ml). The combined organic phases are washed with H_2O, satd. $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated in vacuo: colourless crystals (184 mg, 94%) (CH_2Cl_2/methanol 1:1).

b) The crude reaction mixture (0.46 mmol) obtained from the ether cleavage with iodotrimethylsilane (without addition of methanol) is added to aqueous acetone (100 ml, 3:1) and worked up as above. After chromatography (silica gel, ether/CH_2Cl_2 1:2, R_f = 0.65) and crystallization **35** (163 mg, 88%) is isolated, m.p. 315–316°C. – IR (KBr): $\tilde{\nu}$ = 2980 (C–H), 1770 (C=O), 1720 (C=O), 1230 (C–O) cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): cf. Table 1. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): cf. Table 1. – MS: *m/z* (%) = 404 (35) [M^+], 348 (100), 229 (28), 228 (17), 165 (45), 115 (38).

$C_{24}H_{20}O_6$ (404.4) Calcd. C 71.27 H 4.98
Found C 70.99 H 4.92

Dimethyl C_2(C_s)-anti-14,anti-19-Dimethoxy-anti-4,anti-9-bis(methylthio)undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane-syn-4,syn-9-dicarboxylate (Atropisomers) (**36**)

a) To a solution of **30** (1.0 g, 2.3 mmol) in dry THF (300 ml) is added under N_2 at 0°C a solution of lithium diisopropylamide (LDA), prepared from diisopropylamine (0.9 ml, 6.2 mmol) and *n*-butyllithium (2.5 ml of a 2.4 M solution in hexane, 6.0 mmol) in THF (30 ml) at –30°C. After stirring at room temp. for 3 h, dimethyl disulfide (0.5 ml, 5.5 mmol) is added in one portion. From the clear solution **36** begins to crystallize. The mixture is stirred for 1 h and concentrated in vacuo to 20 ml. The resultant solid material is sucked off and dissolved in CH_2Cl_2 (100 ml). The solution is washed with 5% HCl (3 × 50 ml) and satd. $NaHCO_3$ solution, dried ($MgSO_4$), filtrated through Al_2O_3 (2.0 g) (neutral), and concentrated in vacuo. The solid residue is crystallized from ether to give **36** (1.1 g, 94%).

b) To a solution of **31** (200 mg, 0.46 mmol) in dry THF (50 ml) is added under N_2 at –78°C a solution of LDA (0.2 ml, 1.4 mmol) [from diisopropylamine (0.2 ml, 1.4 mmol) and *n*-butyllithium (0.58 ml of a 2.4 M solution in hexane, 1.4 mmol)], and the mixture is stirred at the same temp. for 5 h. The reaction is quenched at –30°C with dimethyl disulfide (0.13 ml, 1.4 mmol) and worked up as above. After crystallization from ether colourless crystals (190 mg, 82%) are obtained, m.p. 261–262°C. – IR (KBr): $\tilde{\nu}$ = 2970 (C–H), 2810 (C–H), 1710 (C=O), 1250 (C–O), 1110 (C–O) cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 3.71 (s, 2 OCH_3), 3.66 (m, 6-H)*, 3.58 (m, 6-, 7-H), 3.56 (m, 14-, 19-H), 3.51 (m, 7-H)*, 3.23 (s, 2 OCH_3), 3.20 (m, 16-H)*, 3.19 (m, 16-, 17-H), 3.15 (m, 17-H)*, 2.78, 2.77, 2.63, 2.62 (m, 3-, 5-, 8-, 10-H), 2.35, 2.30 (m, 13-, 15-, 18-, 20-H), 2.16 (s, 2 SCH_3). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 171.3 (2 CO_2CH_3), 92.8 (C-14, -19), 69.5 (C-4, -9), 62.5, 62.3, 62.1, 61.8 (C-1, -2, -11, -12), 58.8, 56.5 (C-6, -7)*, 57.7 (C-6, -7), 57.2 (2 OCH_3), 55.8, 55.3 (C-16, -17), 55.5 (C-16, -17), 51.9 (2 OCH_3), 47.6, 47.5, 46.9, 46.6 (C-4, -5, -8, -10), 44.3, 44.2, 44.1 (C-13, -15, -18, -20), 14.4 (2 SCH_3).

anti-14,anti-19-Dimethoxyundecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane-4,9-dione (**37**): A mixture of **36** (1.1 g, 2.2 mmol) and KOH (600 mg, 10.7 mmol) in ethylene glycol (60 ml) is heated to reflux under N_2 for 24 h and then concentrated in vacuo to ca. 10 ml. At room temp., acetic acid (0.63 ml, 11.0 mmol) and methanol (100 ml) are added, the mixture is stirred for 10 min and then $NaHCO_3$ (1.3 g, 15.5 mmol) is added. After additional 15 min it is diluted with methanol/CH_2Cl_2 (1:1) (100 ml), then *N*-chlorosuccinimide (1.18 g, 8.8 mmol) is added and the mixture stirred at room temp. for 4–6 h (total conversion, TLC monitoring). Concentration leaves a solid residue, which is dissolved in CH_2Cl_2 (200 ml). The solution is washed repeatedly with 50% NaCl solution and stirred with conc. HCl (100 ml) for 16 h to give an emulsion. The organic phase is washed with satd. $NaHCO_3$ solution (2 × 50 ml), dried ($MgSO_4$), and concentrated. The solid residue is crystallized from CH_2Cl_2/ether (1:1) to give **37** (280 mg, 39%). Filtration of the mother liquor through Al_2O_3 (2.0 g, neutral, ethyl acetate) and crystallization provide additional 350 mg (49%, total yield 88%), colourless crystals, m.p. 219–220°C. – IR (KBr): $\tilde{\nu}$ = 2980 (C–H), 2960 (C–H), 2890 (C–H), 1760 (C=O), 1105 (C–O) cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): cf. Table 1. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): cf. Table 1. – MS: *m/z* (%) = 348 (49) [M^+], 292 (21), 145 (23), 131 (16), 115 (34), 103 (28), 75 (100).

syn-4,syn-9,anti-14,anti-19-Tetramethoxyundecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane (**38b**): To a suspension of $LiAlH_4$ (20 mg, 0.52 mmol) in dry THF (10 ml) a solution of **37** (100 mg, 0.29 mmol) in THF (2 ml) is added slowly under N_2. The mixture is heated to reflux for 1 h, then H_2O (0.02 ml), aqueous NaOH (0.02 ml, 15%), and H_2O (0.06 ml) are cautiously added, and the mixture is stirred at room temp. until complete decolouration of the greyish suspension. After addition of CH_2Cl_2 (20 ml) and $MgSO_4$ (50 mg) the inorganic salts are removed by filtration, and the residue is washed repeatedly with CH_2Cl_2. After concentration in vacuo the colourless solid (98 mg, 96%) is suspended in dry THF (10 ml) and methyl iodide (125 mg, 0.87 mmol) and added dropwise to a suspension of sodium hydride (21 mg NaH, 80% in mineral oil, 0.7 mmol; repeatedly washed with *n*-hexane) in THF (10 ml) and stirred at room temp. for 24 h. Excess of sodium hydride is hydrolyzed by addition of H_2O (10 ml), the aqueous phase (3 × 20 ml) washed with CH_2Cl_2, and the combined organic phases are dried ($MgSO_4$) and concentrated. Crystallization from hexane gives 96 mg (87%) of **38b**, m.p. 155–156°C. – IR (KBr): $\tilde{\nu}$ = 2960 (C–H), 2850 (C–H), 2815 (C–H), 1110 (C–O), 1100 (C–O) cm^{-1}. – ^1H NMR ($CDCl_3$): cf. Table 1. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): cf. Table 1. – MS: *m/z* (%) = 380 (100) [M^+], 365 (4), 348 (6), 333 (4), 189 (12), 159 (15), 75 (32).

anti-14,anti-19-Diacetoxyundecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane-4,9-dione (**40c**): A solution of **37** (100 mg, 0.29 mmol) in HBr/acetic acid (5 ml, 33%) and acetic anhydride (5 ml) is heated in a closed tube (slight excess pressure) to 120°C for 16 h. The volatile components are distilled off in vacuo to a large extent, the residue is dissolved in CH_2Cl_2 (30 ml) and the solution washed with H_2O (3 × 20 ml) and satd. $NaHCO_3$ solution (3 × 20 ml), dried ($MgSO_4$), and concentrated. Chromatography of the residue on silica gel (ether/CH_2Cl_2 1:2) gives 75 mg of an oily mixture. From ether/hexane **40c** (60 mg, 51%), colourless crystals, m.p. 302–304°C, are obtained. – IR (KBr): $\tilde{\nu}$ = 2990 (C–H), 1760 (C=O), 1730 (C=O), 1250 (C–O) cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.94 (m, 14-, 19-H), 3.51 (m, 16-, 17-H), 3.36 (m, 6-, 7-H), 2.65 (m, 13-, 15-, 18-, 20-H), 2.32 (m, 3-, 5-, 8-, 10-H), 2.05 (s, 2 $OCOCH_3$). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 208.8 (C-4, -9), 170.3 (2 $OCOCH_3$), 85.8 (C-14, -19), 59.9 (C-1, -2, -11, -12), 57.2 (C-16, -17), 47.5 (C-6, -7), 45.4 (C-3, -5, -8, -10), 44.8 (C-13, -15, -18, -20), 20.9 (2 CH_3).

$C_{24}H_{20}O_6$ (404.4) Calcd. C 71.27 H 4.99
Found C 71.05 H 5.03

anti-14,anti-19-Dihydroxyundecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane-4,9-dione (**40a**): A solution of **40c** (50 mg, 0.12 mmol) and K_2CO_3 (5 mg, 0.03 mmol) in dry methanol (20 ml) is stirred at room temp. for 16 h. After addition of a cation exchanger (AG 50W-X8, 100–200 mesh, hydrogen form, 100 mg)

the solution is stirred till it becomes slightly acidic (pH 5–6). Filtration, drying, and concentration in vacuo (10^{-1} Torr) leaves a scarcely soluble, colourless powder. This is used for the subsequent oxidation. After crystallization from CH_2Cl_2/methanol colourless crystals of **40a** (35 mg, 91%), m.p. >320°C, are obtained. – IR (KBr): $\tilde{\nu}$ = 3450 (OH), 2950 (C–H), 1760 (C=O) cm^{-1}. – ^1H NMR ([D$_6$]DMSO, 400 MHz): δ = 3.97 (m, 14-, 19-H), 3.46 (m, 16-, 17-H), 3.31 (m, 6-, 7-H), 2.24 (m, 13-, 15-, 18-, 20-H), 2.15 (m, 3-, 5-, 8-, 10-H). – ^{13}C NMR ([D$_6$]DMSO, 100.6 MHz): δ = 207.0 (C-4, -9), 83.4 (C-14, -19), 59.7 (C-1, -2, -11, -12), 56.7 (C-16, -17), 47.1 (C-6, -7), 46.9 (C-13, -15, -18, -20), 45.2 (C-3, -5, -8, -10).

$C_{20}H_{16}O_4$ (320.3) Calcd. C 74.98 H 5.03
Found C 75.39 H 4.82

Collins Oxidation of **40a**: To a mixture of dry pyridine (0.24 ml, 3.0 mmol) and dry CH_2Cl_2 (20 ml), CrO_3 (150 mg, 1.5 mmol, powdered and dried in vacuo) is added with stirring with exclusion of moisture. The mixture is stirred for additional 10 min. To this homogeneous, deep red solution the crude **40a** (ca. 0.12 mmol) is added. After stirring at room temp. for 1 h, the solution is decanted from the black, tarry residue and the latter washed with CH_2Cl_2 (50 ml). The combined organic phases are filtered through florisil (2 cm; the florisil is washed with 20 ml of dry ether) and concentrated in vacuo to give 40 mg of raw material, consisting mainly of hydrates of **41**.

Acetal Formation: 40 mg of the scarcely soluble oxidation product is suspended in methanol/benzene (1:1) (20 ml) and, after addition of *p*-toluenesulfonic acid (10 mg), heated to reflux for 48 h. The mixture is then diluted with CH_2Cl_2 (20 ml), washed (2 × 10 ml satd. $NaHCO_3$ solution), dried ($MgSO_4$), and concentrated. Chromatography of the residue on silica gel (CH_2Cl_2/ether 2:1; R_f = 0.46) gives a crystalline mixture of bisacetals **43b** and **44b** (7:4, 35 mg, 74%).

C_{2h}-Undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]-icosane-4,9,14,19-tetrone 9,19-Bis(dimethyl acetal) (**43b**): ^1H NMR ($CDCl_3$, 400 MHz): δ = 3.18 (m, 6-, 7-, 16-, 17-H), 3.28 (s, 2 OCH_3), 3.07 (s, 2 OCH_3), 2.63 (m, 3-, 5-, 13-, 15-H), 2.28 (m, 3-, 5-, 18-, 20-H). – MS: i.a. *m/z* (%) = 409 (26), 408 (100) [M^+], 393 (46), 254 (91).

C_{2v}-Undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]-icosane-4,9,14,19-tetrone 14,19-Bis(dimethyl acetal) (**44b**): A solution of **40c** (50 mg, 0.12 mmol) in methanol (20 ml), after addition of *p*-toluenesulfonic acid (10 mg, 0.06 mmol), is heated to reflux for 48 h (TLC monitoring, CH_2Cl_2/ether/methanol 3:2:1). The solution, after addition of K_2CO_3 (10 mg, 0.07 mmol), is concentrated in vacuo. The residue is dried (10^{-1} Torr, P_2O_5), suspended in CH_2Cl_2 (10 ml) and treated with Collins reagent analogously to **40a**. Workup and chromatography on silica gel (CH_2Cl_2/ether 2:1; R_f = 0.46) give **44b** (43 mg, 88% based on **40c**), colourless crystals, m.p. >320°C. – IR (KBr): $\tilde{\nu}$ = 2954 (C–H), 1760 (C=O) cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): cf. Table 1. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): cf. Table 1. – MS: i.a. *m/z* (%) = 409 (27), 408 (100) [M^+], 393 (45), 254 (97), 203 (30).

$C_{24}H_{24}O_6$ (408.4) Calcd. C 70.57 H 5.92
Found C 70.49 H 5.98

(1α,2β,3α,6α,7β,8α)-syn-11,anti-12-Dimethoxy-4,5-benzotetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene (**48**): Cf. **10b**. Colourless crystals, m.p. 71–73°C (methanol). – IR (KBr): $\tilde{\nu}$ = 3070 (arC–H), 3020 (arC–H), 3010 (arC–H), 2990 (C–H), 2970 (C–H), 2920 (C–H), 2890 (C–H), 1175 (C–O) cm^{-1}. – UV (CH_3CN): λ_{max} (ε) = 278 nm (680), 272 (720), 266 (540, sh). – ^1H NMR ($CDCl_3$): δ = 7.05, 6.97 (AA′BB′, 3′-, 4′-, 5′-, 6′-H), 4.66 (m, 9-, 10-H), 3.96 (m, 12-H), 3.39 (m, 3-, 6-H), 3.22 (s, OCH_3), 3.18 (s, OCH_3), 2.89 (m, 11-H), 2.88 (m, 2-, 7-H), 2.60 (m, 1-, 8-H).

$C_{18}H_{20}O_2$ (268.3) Calcd. C 80.56 H 7.51
Found C 80.29 H 7.35

(1α,2β,3α,6α,7β,8α)-anti-11,syn-12-Dimethoxy-4,5;9,10-dibenzotetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene (**49**): Cf. **17**. Colourless crystals, m.p. 121°C (methanol). – IR (KBr): $\tilde{\nu}$ = 3060 (arC–H), 3040 (arC–H), 3020 (arC–H), 2960 (C–H), 2920 (C–H), 2870 (C–H), 2820 (C–H), 1100 (C–O) cm^{-1}. – UV (isooctane): λ_{max} (ε) = 287 nm (310), 265 (1150), 257 (950), 229 (3200). – ^1H NMR ($CDCl_3$): δ = 6.60 (m, 3′-, 3″-, 4′-, 4″-, 5′-, 5″-, 6′-, 6″-H), 3.98 (m, 12-H), 3.41 (m, 3-, 6-H), 3.31 (s, OCH_3), 3.31 (m, 1-, 8-H), 3.13 (m, 2-, 7-H), 3.07 (s, OCH_3), 3.04 (m, 11-H). – ^{13}C NMR ($CDCl_3$, 20.2 MHz): δ = 141.6 (C-9, -10)*, 140.5 (C-4, -5)*, 126.2 (C-4′, -4″, -5′, -5″), 124.8 (C-3′, -6′), 124.3 (C-3″, -6″), 101.7 (C-11)**, 97.1 (C-12)**, 56.8 (OCH_3), 56.3 (OCH_3), 49.2 (C-1, -8)***, 48.1 (C-3, -6)***, 38.7 (C-2, -7).

$C_{22}H_{22}O_2$ (318.4) Calcd. C 82.98 H 6.96
Found C 82.72 H 6.95

syn-15,anti-19-Dimethoxyoctacyclo[12.5.1.0^{2,7}.0^{2,13}.0^{7,18}.0^{8,13}.0^{8,16}.0^{17,20}]icosa-3,5,9,11-tetraene (**50**): Cf. **19**. Colourless crystals, m.p. 134–135°C (*n*-hexane). – IR (KBr): $\tilde{\nu}$ = 3020 (arC–H), 2990 (C–H), 2960 (C–H), 2840 (C–H), 1100 (C–O) cm^{-1}. – UV (isooctane): λ_{max} (ε) = 286 nm (2100), 272 (2200), 261 (2300). – ^1H NMR ($CDCl_3$): δ = 5.77 (AA′BB′, 4-, 5-, 10-, 11-H), 5.32 (AA′BB′, 9-, 12-H), 5.21 (AA′BB′, 3-, 6-H), 4.13 (m, 19-H), 4.01 (m, 15-H), 3.34 (s, OCH_3), 3.26 (s, OCH_3), 2.78 (m, 17-, 20-H), 2.56 (m, 14-, 16-H), 2.28 (m, 1-, 18-H). – ^{13}C NMR ($CDCl_3$, 20.2 MHz): δ = 125.8 (C-10, -11)*, 125.6 (C-4, -5)*, 123.6 (C-3, -6)*, 122.8 (C-9, -12)*, 89.8 (C-15)*, 89.4 (C-19), 63.4 (C-8, -13), 60.6 (C-6, -7), 57.5 (OCH_3), 57.5 (OCH_3), 56.1 (C-1, -18)*, 55.7 (C-14, -16)*, 49.0 (C-17, -20).

$C_{22}H_{22}O_2$ (318.4) Calcd. C 82.98 H 6.96
Found C 83.15 H 6.85

syn-16,anti-21-Dimethoxyundecacyclo[11.9.0.0^{1,6}.0^{2,14}.0^{2,20}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,17}.0^{15,19}.0^{18,22}]docos-10-ene-anti-4,anti-5-dicarboxylic Anhydride (**51**): Cf. **23**. Colourless crystals, m.p. 222–223°C. – IR (KBr): $\tilde{\nu}$ = 2960 (C–H), 2910 (C–H), 2880 (C–H), 1885 (C=O), 1780 (C=O), 1630 (C=O), 1220 (C–O), 1100 (C–O) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 6.07 (m, 10-, 11-H), 3.73 (m, 21-H), 3.60 (m, 16-H), 3.28 (s, OCH_3), 3.04 (m, 4-, 5-H), 3.04 (s, OCH_3), 2.96 (m, 18-, 19-H), 2.74 (m, 9-, 12-H), 2.41 (m, 3-, 6-H), 2.36 (20-, 22-H), 2.32 (m, 15-, 17-H), 2.05 (m, 7-, 8-H). – ^{13}C NMR ($CDCl_3$, 20.2 MHz): δ = 173.6 (2 C=O), 128.8 (C-10, -11), 90.9, 89.2 (C-16, -21), 61.1, 54.0 (C-1, -2, -13, -14), 57.4, 55.5 (2 OCH_3), 53.4 (C-18, -19), 46.2, 45.0, 44.6 (C-7, -8, -15, -17, -20, -22), 38.6, 38.5, 33.2 (C-3, -4, -5, -6, -9, -12). – MS: *m/z* (%) = 416 (100) [M^+], 171 (22), 146 (72).

(1α,2β,3α,6α,7β,8α,9α,14α)-syn-16-tert-Butoxy-syn-15-methoxy-4,5-benzopentacyclo[6.6.1.1^{3,6}.0^{2,7}.0^{9,14}]hexadeca-4,10,12-triene (**52**): Cf. **15**. Colourless crystals, m.p. 149°C (*n*-hexane). – IR (KBr): $\tilde{\nu}$ = 3020 (arC–H), 2960 (C–H), 2930 (C–H), 2880 (C–H), 2800 (C–H), 1110 (C–O) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.19, 7.10 (AA′BB′, 3′-, 4′-, 5′-, 6′-H), 5.45 (AA′BB′, 11-, 12-H), 5.16 (AA′BB′, 10-, 13-H), 4.08 (m, 15-H), 3.55 (m, 16-H), 3.34 (s, OCH_3), 3.21 (m, 2-, 7-H), 3.10 (m, 3-, 6-H), 2.00 (m, 1-, 8-H), 1.88 (m, 9-, 14-H), 1.17 [s, $OC(CH_3)_3$].

$C_{25}H_{30}O_2$ (362.5) Calcd. C 82.83 H 8.34
Found C 82.69 H 8.36

CAS Registry Numbers

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42-0 / **13**: 131974-43-1 / **14**: 132017-41-5 / **15**: 122133-98-6 / **16**: 131974-44-2 / **17**: 122133-99-7 / **18**: 131974-45-3 / **19**: 122134-00-3 / **23**: 122134-01-4 / **24**: 131974-47-5 / **25**: 122134-02-5 / **26**: 131974-48-6 / **27**: 131974-49-7 / **28**: 122134-03-6 / **30**: 122134-05-8 / **31**: 122210-81-5 / **32a**: 122134-06-9 / **32c**: 131974-46-4 / **33**: 124316-55-8 / **34**: 124316-49-0 / **35**: 122134-07-0 / **36**: 122134-08-1 / **37**: 122134-09-2 / **38b**: 131974-50-0 / **40a**: 131974-51-1 / **40c**: 122134-10-5 / **41**: 122134-14-9 / **43b**: 131974-52-2 / **44b**: 122134-13-8 / **48**: 132074-34-1 / **49**: 132074-35-2 / **50**: 132074-36-3 / **51**: 132074-37-4 / **52**: 131974-53-3 / maleic anhydride: 108-31-6

☆ Dedicated to Professor *Hans Georg von Schnering* on the occasion of his 60th birthday.

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